

N.N.LEBEDEV

**CHEMISTRY
AND
TECHNOLOGY
OF BASIC
ORGANIC
AND
PETROCHEMICAL
SYNTHESIS**

2

**MIR PUBLISHERS
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Н.Н.ЛЕБЕДЕВ
ХИМИЯ И ТЕХНОЛОГИЯ
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CHAPTER 5

SULPHATION, SULPHONATION AND NITRATION PROCESSES

Sulphation includes reactions leading to the formation of esters of sulphuric acid—alkyl sulphates, ROSO_2OH . By contrast, *sulphonation* gives sulphonic acids (RSO_2OH or ArSO_2OH) and also their derivatives, in which the sulphur atom is directly attached to a carbon atom. *Nitration* consists of the synthesis of nitro compounds (RNO_2 or ArNO_2), in which the nitrogen atom is linked to a carbon atom directly rather than via an oxygen atom, as is the case with nitro esters, RONO_2 . Sulphation is a special case of esterification reactions considered earlier, but it has a number of common features with the sulphonation of organic compounds. Nitration in turn has something in common with sulphonation. This is why all these processes are considered in one chapter.

The processes to be described in this chapter are of great practical significance. Alkyl sulphates and alkyl and aryl sulphonates are the most widely used synthetic surface-active agents (surfactants). Nitro compounds are used for the production of amines, isocyanates, pesticides, etc. Many of these compounds are produced on a large scale. For example, in the USA the forecast for 1980 was $\approx 1,300,000$ tons of anionic surfactants of the type of alkyl sulphates and alkyl and aryl sulphonates, 600,000 tons of nitrobenzene, and 400,000 tons of dinitrotoluene.

5.1. Sulphation of Alcohols and Olefins. Surfactants of the Alkyl Sulphate Type

5.1.1. Chemistry and Scientific Foundations

Sulphation of Alcohols. This reaction is employed chiefly for the production of surfactants of the alkyl sulphate type; it can be effected by using sulphuric, chlorosulphonic and sulphamic acids and also sulphuric anhydride.

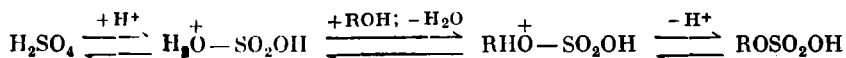
The traditional process is the interaction of alcohols with sulphuric acid, which is a reversible esterification reaction:



By thermodynamic characteristics it is similar to the esterification by carboxylic acids. For example, with the equimolar ratio of the reagents the equilibrium degree of conversion of primary alcohols is ≈ 65 percent; it decreases to 40-45 percent for secondary alcohols and becomes very low for tertiary alcohols. The reactivity of alcohols varies in the same direction: for primary alcohols it is about 10 times higher than for secondary alcohols. In contrast to esterification by carboxylic acids, sulphation reactions are strongly exothermic, but this is due mainly to the heat evolved when sulphuric acid is diluted with alcohol and the water formed. Because of this, the heat effect depends on the concentration of sulphuric acid and on its molar sulphuric acid-alcohol ratio. For instance, for the reaction of 1 mole of alcohol with 1.9 moles of 100-percent sulphuric acid the heat effect is 117 kJ/mol (28 kcal/mol).

The equilibrium degree of conversion of alcohol can be increased by using the concentrated acid (98-100-percent) in an excess with respect to the alcohol [(1.8-2.0):1], in which case the yield of primary alkyl sulphates amounts to 80-90 percent. It has also been suggested that the water formed be distilled off with the aid of azeotrope-forming substances (CCl_4) or in vacuum.

The mechanism of the sulphation of alcohols by sulphuric acid is in general analogous to the esterification processes considered earlier. The acid acts both as a reagent and a catalyst and the reaction proceeds with rupture of the S—O bond, which is why no isomerization occurs in the alkyl group:



This mechanism may be described by the following kinetic equation:

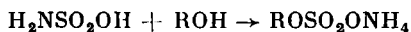
$$r = k_1 h_0 \{ [\text{H}_2\text{SO}_4][\text{ROH}] - \frac{1}{K} [\text{ROSO}_2\text{OH}][\text{H}_2\text{O}] \}$$

which, however, becomes complicated because of the formation of sulphuric acid hydrates. In spite of the high acidity of the medium (h_0), the reaction proceeds relatively slowly (1-3 hours) and is slowed down by the water formed. In the sulphation of higher alcohols, which are difficultly soluble in sulphuric acid, the reaction is retarded by diffusion, which is why intensive stirring is required.

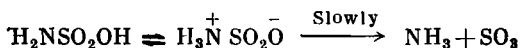
Sulphation gives a number of by-products. For example, the dehydrating action of sulphuric acid results in the formation of olefins, the yield of which increases for secondary and especially for tertiary alcohols. The oxidizing action of sulphuric acid leads to the formation of aldehydes and ketones, which are capable of undergoing further resinification and condensation (in the production of surfactants the product becomes dark and its quality is impaired). Since the amount of olefins and carbonyl compounds formed increases

with increasing temperature, the principal way for suppressing the undesirable side reactions is to keep the temperature within the range of 20-40 °C. For the same reason, oleum must not be used as a sulphating agent.

With other sulphating agents the reaction becomes irreversible. When sulphamic acid is used, the reaction proceeds according to the equation:

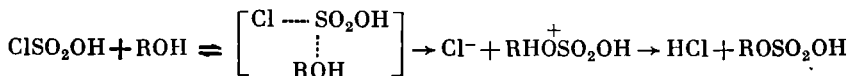


and is first-order with respect to sulphamic acid and zero-order with respect to the alcohol. This shows that the rate-limiting step is some conversion in the acid molecule, possibly its decomposition into ammonia and sulphuric anhydride:

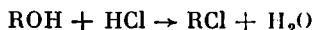


Sulphamic acid is but slightly active as a sulphating agent and has a "mild" action: its reaction with alcohols proceeds at 100-125 °C. Because of the relatively high cost sulphamic acid is used only in special cases (the sulphation of ethoxylated phenols and unsaturated alcohols), where other sulphating agents give an undesirable mixture of products.

Chlorosulphonic acid has found wide application for the sulphation of alcohols. Like other acid chlorides, it is highly reactive—the reaction occurs at a high rate even at room temperature, is first-order in acid and alcohol and involves the attack of the alcohol molecule on the sulphur atom:

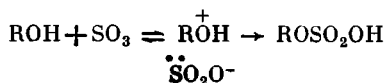


In spite of the high activity, chlorosulphonic acid has a "mild" action and the reaction proceeds with an almost theoretical yield. The amount of chloro derivatives increases with increasing temperature, especially in the sulphation of secondary alcohols:



The formation of chloro derivatives can be repressed by lowering the temperature and removing HCl rapidly.

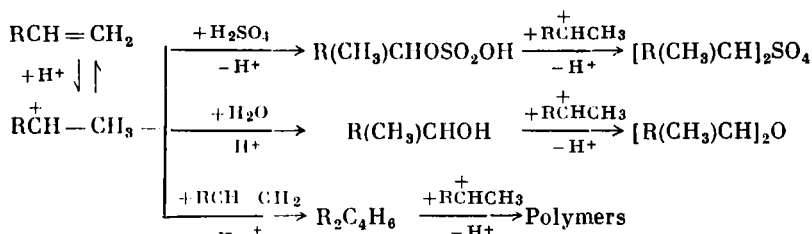
Sulphuric anhydride has lately assumed importance as a sulphating agent. Its electrophilic properties are due to the presence of vacant orbitals; it can combine with the oxygen atom of the alcohol, forming a complex, which is then converted to an alkylsulphuric acid:



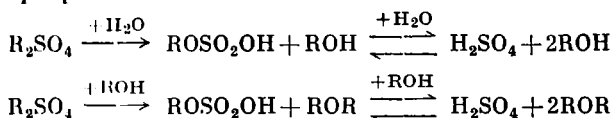
The chemical reaction itself occurs almost instantaneously and when gaseous sulphuric anhydride is used, the reaction rate is limited by its diffusion, and the process is completed in the boundary film of the liquid phase. Because of the high exothermicity of the reaction, this can lead to local overheating and to the formation of by-products (olefins, carbonyl compounds, resins), which cause a darkening of the surfactants obtained and lower their quality. Therefore, the method of carrying out the reaction is important: the heat evolved must be removed, local overheating prevented and a reliable temperature control provided (by diluting SO_3 with an inert gas, intensive stirring and by carrying out the reaction in the film).

Sulphation of Olefins. This reaction has already been encountered in connection with the sulphuric-acid method of separation of isobutylene from the C_4 fractions (page 58) and with the sulphuric-acid hydration of olefins (page 200). The reaction is carried out by using only sulphuric acid since other sulphating agents are either inactive or give products other than sulphates.

The reaction of olefins with H_2SO_4 proceeds with the sequential formation of mono- and dialkyl sulphates and olefinic polymers; if sulphuric acid contains water, an alcohol and an ether are also formed. The reaction occurs via the intermediate formation of a carbonium ion:



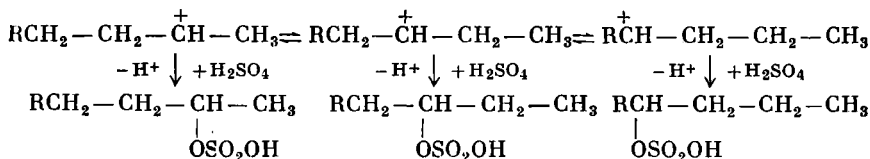
Moreover, an alcohol and an ether are formed as a result of the reversible reactions of hydrolysis and alcoholysis of a monoalkyl sulphate and especially of a dialkyl sulphate, which has strong alkylating properties:



The reaction also involves the formation of oxidation products and resinous compounds (as a result of condensation), which lower the quality of surfactants. Since the major end product is monoalkyl sulphate, the molar ratio of olefin to H_2SO_4 taken invariably in practice is close to 1:1. In order to avoid excessive olefin polymerization, resinification and also the formation of a dialkyl sulphate and

an ether, use is made of commercial (92-93-percent) sulphuric acid (oil of vitriol) and a temperature of 0-40 °C.

The addition of sulphuric acid to olefins occurs in accordance with Markovnikov's rule; normal olefins give secondary alkyl sulphates. It is known that carbonium ions are capable of undergoing rapid isomerization with the transfer of hydride ions but with the retention (under moderate reaction conditions) of the carbon skeleton of the molecule. Therefore, higher *n*-olefins give a mixture of secondary alkyl sulphates with different positions of the sulphotoester group:



The reaction of *n*-olefins with sulphuric acid under moderate reaction conditions is practically irreversible and highly exothermic ($-\Delta H_{298}^\circ = 88 \text{ kJ/mol}$ or 21 kcal/mol).

With the rate-limiting step of formation of a carbonium ion the kinetics of the reaction is described by the following equations:

$$r = kh_0 [\text{Olefin}]$$

It can be seen that the reaction rate increases with increasing acidity of the medium (h_0), which is strongly dependent on the concentration of sulphuric acid. Olefins are insoluble in the acid, which is why the diffusion retardation of the process is important when the molecule is transferred from the hydrocarbon to the sulphuric-acid phase, which can (together with heat removal) limit the overall rate of the reaction. It has been reported that the process can be effected through intensive stirring and heat transfer in about 1 min (the usual reaction time is about 1 hour).

5.1.2. Technology of Sulphation

Surfactants of the alkyl sulphate type may be divided into three principal groups.

1. Primary alkyl sulphates obtained from primary alcohols with a linear carbon chain. These alcohols are partly products of the hydrolysis of natural fats and are called fatty alcohols (say, lauryl alcohol, $\text{C}_{12}\text{H}_{25}\text{OH}$, and myristyl alcohol, $\text{C}_{14}\text{H}_{29}\text{OH}$), but they are mainly synthesized by the hydrogenation of higher fatty acids prepared by the oxidation of paraffin wax, organoaluminium synthesis or Oxo synthesis. In the last three cases, the raw materials are mixtures of primary alcohols with a suitable length of the alkyl group.

ders. They are used for the laundering of clothes and fabrics, for the washing of wool, various articles, etc.

Sulphation by Sulphuric Acid. The sulphations of alcohols and olefins by sulphuric acid intended for the production of surfactants have many features in common. Both reactions are carried out at a low temperature (0-40 °C), with intensive cooling with brine and stirring, which is needed for the removal of diffusional retardation

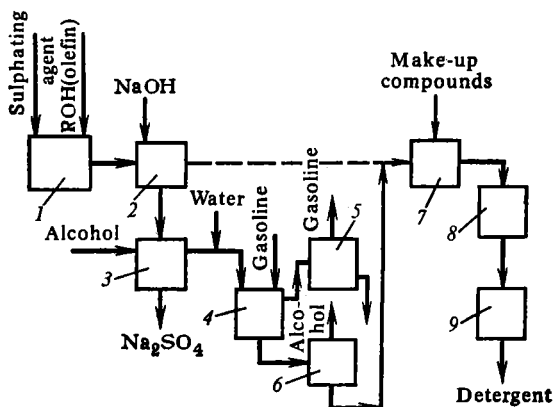
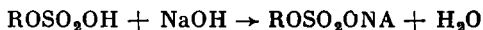


Fig. 5.1. Basic processes in the production of surfactants of the alkyl sulphate type:

1—sulphation; 2—neutralization; 3—separation of Na_2SO_4 ; 4—extraction; 5—regeneration of gasoline and recovery of the unconverted organic reagent; 6—recovery of the alcohol-solvent; 7—mixing with other components of the detergent; 8—drying; 9—crushing and packing.

and to intensify heat exchange. In the batch process, use is made of a stirred reactor and alcohol or olefin is gradually added to the acid. Just as in the synthesis of any surfactants, the reaction mixture becomes thickened, which makes difficult its stirring and cooling. In the continuous synthesis, use is made of cascades of stirred reactors, screw-conveyer units, etc.

In the sulphation of alcohols the resulting mass contains mainly alkylsulphuric acid; unconverted sulphuric acid and alcohol are also present. When olefins are sulphated, the mixture also contains unconverted olefin and a small amount of dialkylsulphuric acid, ether and polymers. The flowsheet of the processing of this mass is shown in Fig. 5.1. The mass is neutralized with concentrated caustic in unit 2, the temperature being kept below 60 °C. The alkylsulphuric acid is converted to a salt:



and the dialkyl sulphate gives the same salt and an alcohol molecule:



and sulphuric acid is converted into sodium sulphate. The mixture is separated into its components in unit 3 by extraction with ethyl or isopropyl alcohol, in which organic compounds and alkyl sulphate are soluble and sodium sulphate is not (it is separated as a waste). The alcoholic solution of the compounds is then diluted with water in unit 4 and the unconverted organic reagents and by-products are extracted in unit 4 by gasoline.

The gasoline is then distilled off from this extract in unit 5 (the residue may be returned to sulphation). The aqueous-alcoholic solution of the alkyl sulphate passes from unit 4 to unit 6, where the alcohol is distilled off, the remaining concentrated aqueous solution of the alkyl sulphate being led to unit 7, where it is mixed with the other components of the detergent (phosphates, soda, carboxymethyl cellulose, bleaching agents). The mixture is led to unit 8 where it is dried and then to unit 9, where it is crushed and packed.

With a simplified flow diagram of the production of a low-quality detergent of the alkyl sulphate type units 3, 4, 5 and 6 are not used, and the neutralized mixture is directly led for stirring and packing or is preliminarily passed to a unit (not shown in the diagram), where the organic compounds are distilled off by superheated steam. Such a detergent contains a large amount of sodium sulphate.

The shortcomings of the production considered above (i.e., the incomplete use of the reagents, the Na_2SO_4 waste formed, and also the technological complexities of the complete processing of the reaction mass for the production of a high-quality detergent) have led to the replacement of the sulphuric-acid sulphation of alcohols by other methods of synthesis of alkyl sulphates.

Sulphation of Alcohols by Chlorosulphonic Acid. The irreversibility and high rate of this reaction make it possible to use an equimolar ratio of the reagents on complete conversion into alkylsulphuric acid. This substantially reduces the consumption of alcohols and sulphating agent. There are practically no side reactions; the only co-product (gaseous HCl) can be used in the form of 20-30-percent hydrochloric acid. Thus, the reaction mass consists mainly of alkylsulphuric acid, and its further processing is simplified and the surfactant obtained does not contain inorganic salts. These advantages have led to the extensive use of chlorosulphonic acid for the sulphation of alcohols.

A specific feature of the sulphation of alcohols by chlorosulphonic acid is the formation of gaseous HCl , which is difficult to remove because of the gradual thickening of the mixture. The use of solvents, vacuum, etc., has been suggested, but the best method is to carry out the reactions in a vessel that provides a large specific surface of the liquid for removal of HCl .

One of such reaction units is shown schematically in Fig. 5.2a. The reactor is fitted with a tray (with a side sleeve), cooling coils

and a stirrer. Chlorosulphonic acid and alcohol are introduced into the centre of the tray and are made to react. The partly reacted mixture flows down through the side sleeve onto the walls cooled by water through the jacket. Here the reaction is completed in a thin film of the dripping liquid and residual HCl is removed. The resulting mass is passed directly to the caustic neutralization unit; the flow diagram of this production includes only units 1, 2, 7, 8 and 9 (see Fig. 5.1) and also an additional HCl utilization unit.

Sulphation of Alcohols by Sulphuric Anhydride. This reaction has the same advantages as the sulphation by chlorosulphonic acid.

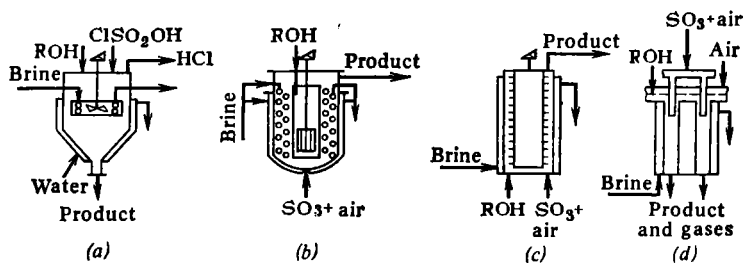


Fig. 5.2. Reaction units for sulphation and sulphonation:

a—unit with a reaction tray (sleeve); b—cascade of reactors with turbomixers; c—unit with a revolving internal drum; d—film reactor.

Moreover, sulphuric anhydride is cheaper than chlorosulphonic acid and does not give HCl and, hence, no HCl utilization unit is needed. Therefore, the sulphation by sulphuric anhydride is today the most promising method and it replaces the other methods.

The main difficulties in the practical realization of the sulphation of alcohols by sulphuric anhydride are a very high rate and high exothermicity of the reaction, as a result of which the reaction mixture can be overheated, side reactions appear and the product can be darkened. The process was improved by using SO_3 vapours diluted with air to a concentration of 4-7 percent (by volume). This considerably slows down the diffusion of SO_3 from the vapour into the liquid phase and makes it possible to solve the problem of heat removal. The large-tonnage production of surfactants by this method may be combined with the unit for the air oxidation of SO_2 and based on the SO_2 -containing effluent gases from metallurgical plants.

The other reaction units used for the sulphation of alcohols by sulphuric anhydride are also shown in Fig. 5.2 (b, c and d).

In one of them (Fig. 5.2b) use is made of a cascade of two or three reactors equipped with turbomixers, cooling coils and jackets. The presence of a cylindrical shell inside the reactor creates a highly turbulent vertical stream of the mixture, which provides intensive circulation and heat removal. The liquid moves successively through

all the reactors and the SO_3 diluted with air is led into each of the reactors.

In another type of reactor (Fig. 5.2c) there is a shell fitted with a cooling jacket and an internal revolving drum; this drum has pins on its external surface, which provide better mixing and vigorous agitation of the reagent stream moving upwards in a narrow circular space between the shell and the drum. This design is rather complicated, which is why film reactors have found wider use.

There are single-tube and multi-tube film reactors (of the type of shell-and-tube heat exchangers with a liquid film running down

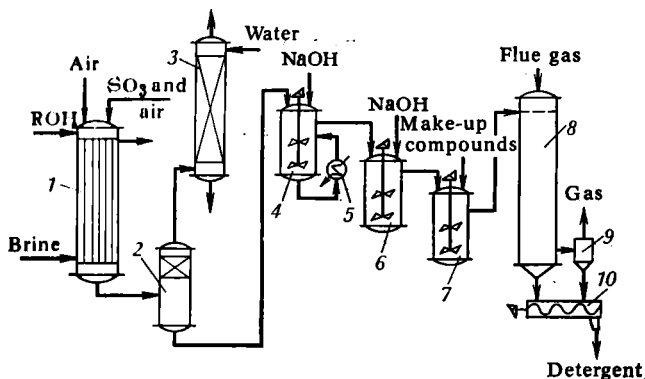


Fig. 5.3. Flow diagram of production of a detergent based on alkyl sulphates: 1—reactor; 2—separator; 3—absorber; 4, 6—neutralization units; 5—cooler; 7—mixer; 8—spray drier; 9—cyclone; 10—screw conveyer.

through the tubes and with cooling by brine or water circulating in the intertube space). Sometimes, film reactors consist of several concentric cylinders: the reagents are introduced into some of the circular spaces formed by them and the cooling water is circulating in the remaining ones (Fig. 5.2d). The organic reagent is introduced at the top through special metering devices, this providing the formation of a uniformly dripping liquid film on the walls. The air-diluted SO_3 is also introduced at the top cocurrently to the liquid; in order to prevent the SO_3 from entering the top of the reactor, air is admitted there, and the diluted SO_3 is led through special pipes lowered into the reaction space.

The flow diagram of the production of detergents based on an alkyl sulphate is given in Fig. 5.3. The alcohol, air and air-diluted SO_3 vapours are continuously introduced into film reactor 1. The effluent gases are separated in separator 2 from the liquid and led into absorber 3 for purification from SO_3 . The resulting alkylsulphuric acid is neutralized with a concentrated caustic soda solution in

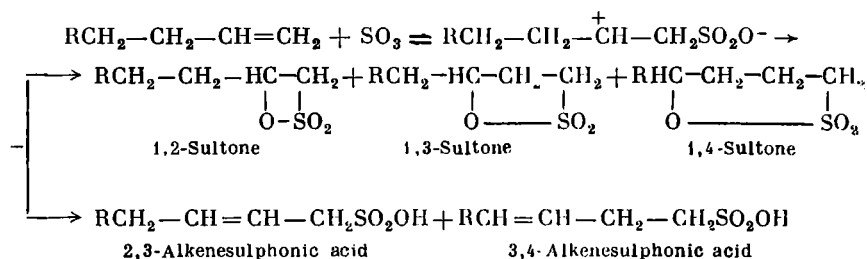
unit 4, which is fitted with a stirrer and an external cooler 5, through which the liquid is pumped. The temperature for neutralization must not exceed 60 °C. The mixture is then additionally neutralized (up to the required pH 7; the control is effected using a special pH-meter) in unit 6 fitted with a stirrer. The neutralized mass, which contains alkyl sulphate and water, is then passed into mixer 7, where the other components are added (phosphates or pyrophosphates, soda, bleaching agents, carboxymethylcellulose). This mixture is pumped into spraying drier 8; it is sprayed through special nozzles into the hot flue gas stream. The solid particles entrained by the gas are trapped in cyclone 9. The powder-like detergent is transferred from the bottom of the drier and cyclone by screw conveyer 10 for packing.

5.2. Sulphonation Processes. Surfactants of the Alkene and Aryl Sulphonate Types

The sulphonation reaction is typical of aromatic compounds, but it has lately assumed practical importance for olefins as well.

5.2.1. Sulphonation of Olefins

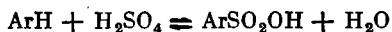
In contrast to the sulphation of olefins by sulphuric acid, the reaction of olefins with oleum or SO₃ leads to sulphonation with the formation of a C—S bond. The electrophilic properties of SO₃ are responsible for the primary formation of a dipolar complex which can be isomerized with the migration of the hydride ion and form a mixture of alkenesulphonic acids and sultones (the inner esters of hydroxysulphonic acids):



Alkenesulphonic acids when neutralized by caustic are converted into the corresponding salts, and 1,2-sultones are converted into the salt of α-hydroxysulphonic acid. 1,3- and 1,4-Sultones are more stable toward hydrolysis, but at elevated temperature they also give hydroxysulphonic acids, which split off water at 130-150 °C and

Chemistry and Scientific Foundations. The sulphonation of aromatic compounds is mainly carried out using sulphuric acid, oleum and SO_3 .

The sulphonation by sulphuric acid is a reversible reaction:

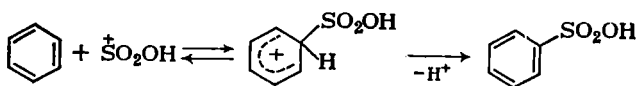
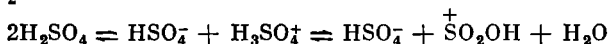


which proceeds with evolution of a considerable amount of heat, including the heat released as a result of the dilution of the acid with the water formed. Because of this, the heat effect depends on the concentration of the acid and is $\approx 146 \text{ kJ/mol}$ (35 kcal/mol). The equilibrium of the reaction under ordinary conditions is shifted to the right, but when the temperature is increased and the hydrocarbon is simultaneously distilled off, a reverse process is sometimes carried out and used for the separation of isomeric alkylbenzenes.

Sulphonation belongs to typical reactions of electrophilic substitution in the aromatic ring. The reaction is retarded by water present in the acid and formed upon sulphonation; the reaction rate is often described by the following equation:

$$r = k \frac{[\text{ArH}]}{[\text{H}_2\text{O}]^n}$$

It is believed that the agent that attacks directly the aromatic ring is the SO_2OH^+ ion:



The formation of by-products during the sulphonation by sulphuric acid is insignificant and depends mainly on the oxidizing action of the acid.

The effect of substituents in sulphonation reactions is the same as in other electrophilic substitutions in the aromatic ring; sulphonation exhibits an average selectivity toward the orientation into the various positions of the molecule and the relative reactivity. For example, toluene is sulphonated 5 times faster than benzene; the product consists of 75 percent of *para*-, 20 percent of *ortho*- and 5 percent of *meta*-toluenesulphonic acids. The electronegative groups considerably deactivate the aromatic ring, which is why a second sulpho group cannot be introduced by the action of sulphuric acid. In regard to the composition of the isomers the sulphonation reaction has certain specific features, which depend on the reversibility of the reactions. Under "mild" conditions the composition of the isomers is determined by the relative reactivity of the various positions of the ring; upon heating or with a long reaction time it depends on the

thermodynamic stability of the isomers. For instance, naphthalene gives mainly 1-sulphonic acid in the first case and the 2-isomer in the second.

Since the sulphonation by sulphuric acid is reversible and the activity of the acid is strongly diminished upon dilution with the water formed, the reaction is usually stopped when a certain concentration of the acid is reached. This phenomenon is characterized by the π -factor of sulphonation. It is numerically equal to that concentration of SO_3 in the spent acid at which the sulphonation no longer proceeds (the value of π is 64 for benzene, 56 for naphthalene, and 82 for nitrobenzene). Knowing the sulphonation π -factor and the concentration of SO_3 in the starting acid (a), one can calculate the amount of acid required for the sulphonation of 1 mole of an aromatic compound using the formula

$$x = 80 \frac{100 - \pi}{a - \pi}$$

where 80 is the molecular mass of SO_3 . The above formula shows that in order to reduce the consumption of H_2SO_4 and the amount of spent acid, use must be made of the maximum possible concentration of sulphuric acid. For example, when benzene is sulphonated ($\pi = 64$) with oil of vitriol (93-percent sulphuric acid; $a = 75$), the minimum amount of oil of vitriol is 262 g, and for the reaction with 100-percent sulphuric acid ($a = 81.7$) it is only 162 g. This gives, respectively, 182 and 82 g of spent acid.

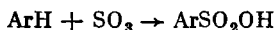
Because of the low activity of sulphuric acid as a sulphonating agent, the process is usually carried out at elevated temperature (80-100 °C and higher). The reaction mass consists of two phases, and the chemical reaction itself occurs in the acid phase and even upon slight stirring it is limited by the rate of the chemical conversion with no substantial effect of diffusion factors.

Sulphonation by Oleum and SO_3 . The reaction of aromatic compounds with oleum occurs in two steps. The first step is the conversion of excess sulphuric anhydride:



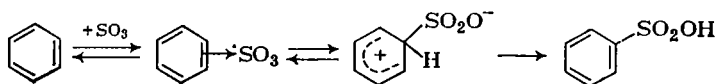
This reaction is irreversible and highly exothermic; its heat effect depends on the oleum concentration, being equal to 180 kJ/mol (43 kcal/mol) for 20-percent oleum. In the second step, sulphuric acid becomes involved in sulphonation (the interaction of sulphuric acid with aromatic compounds has been described above).

The sulphonation by free sulphuric anhydride



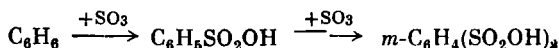
also proceeds irreversibly and is one of the strongest exothermic reactions of organic synthesis ($-\Delta H_{298}^\circ = 217 \text{ kJ/mol}$ or 52 kcal/mol).

The mechanism of the first step of the sulphonation of aromatic hydrocarbons by oleum and of their reactions with SO_3 consists of the electrophilic attack on the hydrocarbon by a molecule of SO_3 via intermediate π - and σ -complexes:



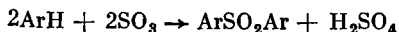
The reaction is first-order in ArH and SO_3 and proceeds almost instantaneously. As a result, with the process being heterophasial the velocity depends on the diffusional factors and to a considerable extent on the intensity of stirring and removal of a large amount of heat evolved.

In contrast to sulphonation using sulphuric acid, the reactions with oleum and SO_3 are accompanied by a large number of side reactions. The high activity of these reagents makes possible the introduction of a second sulpho group into the aromatic ring according to the typical scheme of sequential conversions:



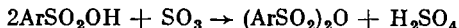
This reaction is used for the synthesis of *m*-benzenesulphonic acid with subsequent formation of resorcinol, when the first step is carried out using H_2SO_4 and the second step is effected by the action of oleum.

The sulphonation by oleum and SO_3 involves the formation of a certain amount of sulphones:



This reaction is especially noticeable in the sulphonation of benzene, but for alkylbenzenes the extent of this reaction is insignificant.

Another side reaction leads to the formation of sulphonic acid anhydrides, the yield of which increases when an excess of SO_3 is used:



The action of a small amount of water can convert the anhydrides into the end sulphonic acids.

The side reactions described above and also the oxidative conversions and degradation of alkyl groups by the action of SO_3 can be limited by using the optimum ratio of the reagents, a suitable mixing operation and especially by choosing a suitable temperature, which usually ranges from -10 to 40 – 60°C when oleum and SO_3 are used for sulphonation.

Process Technology. One of the key problems in the sulphonation of aromatic compounds is the complete use of the sulphonating

agent without the formation of its wastes in the form of diluted acid or salts. Besides, the presence of these compounds in the sulpho mass complicates the technology, requiring the separation of the end product.

When the sulphonation is carried out using sulphuric acid, this problem is solved most simply for sufficiently volatile aromatic hydrocarbons, when the water formed can be distilled off as an azeotropic mixture with the unconverted hydrocarbon. This method, which is

called the "in-vapour" sulphonation, is especially widely employed for the sulphonation of benzene and toluene. It is also recommended for the sulphonation of high-boiling compounds, in which case there must be introduced a foreign agent with which the water can be removed in the form of an azeotropic mixture. Sometimes, water is removed in the absence of such an agent provided that the process is effected at a sufficiently high temperature or in vacuum.

The in-vapour sulphonation by sulphuric acid is commonly carried out at a higher temperature (160-180 °C) required for the more complete removal of water.

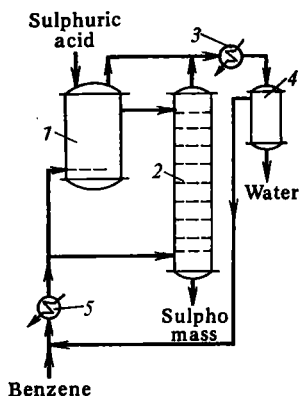


Fig. 5.4. Flow diagram of sulphonation of benzene "in vapours":

1, 2—reactors; 3—cooler-condenser; 4—separator; 5—vaporizer.

This process can be accomplished in batches or continuously. The reaction unit for the continuous sulphonation of benzene "in vapours" is shown schematically in Fig. 5.4.

Fresh and recycle benzene is vaporized and overheated in unit 5 and led to reactor 1 through a bubbler. Sulphuric acid (in the form of oil of vitriol with 90-93 percent H_2SO_4) is continuously introduced into the same reactor. The reactor has neither heat-exchange surface nor stirrer (their functions are performed by the benzene vapours bubbling through the reaction mass and introduced in a 4- to 6-fold excess). The liquid from reactor 1 overflows into reaction column 2, into the lower part of which are led the benzene vapours moving countercurrently to the liquid. The column has cap trays, on which the sulphonation occurs in a layer of the reaction mass. The composition of the sulpho mass varies upon its downward movement: it becomes increasingly enriched with benzenesulphonic acid and impoverished in sulphuric acid. From the still of column 2 the sulpho mass is led for further processing. The benzene vapours from units 1 and 2 are condensed together with the entrained water vapours in

cooler-condenser 3 and the condensate is separated in separator 4 into the aqueous and benzene layers. The benzene layer is neutralized (the neutralization unit is not shown in Fig. 5.4) and recycled to the process.

Another method of a more complete use of SO_3 employs oleum for the sulphonation of aromatic compounds. Oleum has a high initial content of SO_3 and, according to the formula given on page 356, its consumption for sulphonation and the formation of waste H_2SO_4 per unit amount of product is lower than in the case of sulphuric acid.

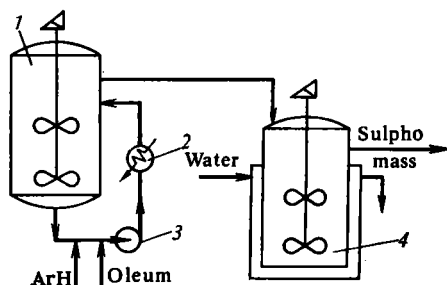


Fig. 5.5. Reaction unit for sulphonation by oleum (fuming sulphuric acid): 1, 4—reactors; 2—external cooler; 3—pump.

The sulphonation by oleum is not infrequently carried out batch-wise; the aromatic hydrocarbon is gradually added to oleum on stirring and cooling but the reaction is brought to completion at elevated temperature. The continuous sulphonation process using oleum for the synthesis of surfactants (Fig. 5.5) is carried out in a cascade consisting of 3 or 4 stirred reactors (only two such reactors are shown in Fig. 5.5). The first, most exothermic step of the complete use of excess SO_3 is carried out in the first reactor fitted with an external brine cooler 2, the oleum and the cooled reaction mass being mixed at the suction line of pump 3. The other reactors operate on cooling with water, but the temperature is gradually increased to provide a more complete use of sulphuric acid.

The amount of the sulphonating agent can be reduced when SO_3 is used. There are two variants of the sulphonation of aromatics by SO_3 . The first is suitable for slightly volatile compounds and involves the sulphonation by SO_3 vapours diluted with air. As far as the reaction conditions and the reactor type are concerned (see Fig. 5.2b, c and d) the process is analogous to the sulphonation of alcohols and olefins by SO_3 . In the second variant, the reaction is effected in liquid sulphur dioxide, in which both SO_3 and the aromatic hydrocarbon are soluble. At the boiling point of liquid SO_2 equal to -10°C the process occurs under mild homogeneous conditions, the heat of

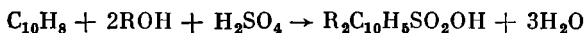
the reaction being removed by the evaporation of SO_2 ; this prevents overheating and reduces the extent of side reactions. This method of sulphonation employs the reactor described earlier for the sulphonation of alcohols by chlorosulphonic acid (see Fig. 5.2a).

Alkyl Aryl Sulphonates. These surfactants have an alkyl group linked to the aromatic nucleus (the hydrophobic portion) and the hydrophilic sulphonate group SO_2ONa . They are divided into two groups: (1) petroleum sulphonates made by the sulphonation of petroleum fractions containing alkylaromatic hydrocarbons; and (2) synthetic sulphonates.

Petroleum alkyl aryl sulphonates are obtained by treatment of various petroleum fractions with oleum. Sometimes they are formed as co-products in the dearomatization of lubricating oils by oleum. The alkylaromatic hydrocarbons contained in petroleum oils have various structures (the length and number of alkyl groups and the presence of condensed rings), which is why the sulphonates made from them are complex mixtures of compounds. Depending on the average molecular mass of the starting oil, sulphonic acids may be water- or oil-soluble.

Petroleum sulphonates exhibit a lower surface activity than synthetic sulphonates, but they are less costly. They have an odour (due to the oil impurity) and are coloured (sometimes, even black). Their use for the production of detergents is therefore limited, but they are extensively used as viscosity additives to lubricating oils, as emulsifying and de-emulsifying agents in the petroleum industry, as flotation agents, etc.

Synthetic alkyl aryl sulphonates (*sulphonols*) are the major synthetic detergents and their production is about 50 percent of the total. The first product of the series, nekal, was produced by treating naphthalene with isopropyl (or isobutyl) alcohol and sulphuric acid. Sulphuric acid plays also the part of an alkylation catalyst and sulphonating agent; two alkyl groups, on an average, are introduced into the ring:

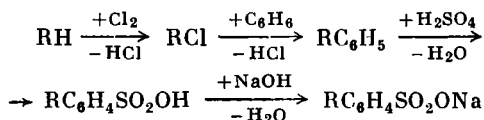


Since products of the type of nekals have a low surface activity, the possibilities of synthesis of surfactants from benzene by its alkylation and sulphonation have been studied. It has been found that the surface-active properties of the alkyl aryl sulphonates obtained depend significantly on the structure of the alkyl chain. For example, with the 1-position of the phenylsulphonate group and a straight alkyl chain, maximum detergent properties are exhibited when the alkyl group contains 11-14 carbon atoms. The position of the phenylsulphonate group in the aliphatic carbon chain is also important. For example, of dodecylbenzene sulphonates having a straight chain of carbon atoms in the alkyl group, the best detergent

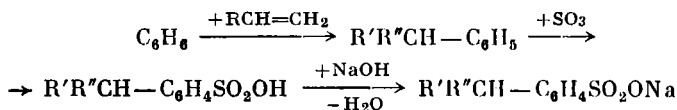
properties are exhibited by 2- and especially 3-isomers, but the detergent quality is lowered with increasing distance of the substituent from the end position.

Branching of the alkyl group with its length remaining the same leads to the impairment of their surface-active properties; the same effect is caused by the presence of two alkyl groups in the ring.

These data show that the best way for the synthesis of alkyl aryl sulphonates is to use alkylbenzenes with C_{10} - C_{16} alkyl groups (most preferably, C_{11} - C_{14} alkyl groups). Because of the biodegradability problem, the degree of branching of the alkyl group must be at a minimum; the use of dodecylbenzene sulphonates obtained from a propylene tetramer has been banned in most countries. At present the best source of the alkyl group is the narrow kerosene fraction of paraffin-base petroleum, soft paraffin wax obtained from fractions with the aid of carbamide or molecular sieves, and also α -olefins made by the cracking of paraffin wax or by organoaluminium synthesis. When paraffins are used, the process consists of the chlorination (page 117), the alkylation of benzene by chloroalkane (page 264) and the sulphonation followed by neutralization:



When α -olefins are used, the process involves alkylation (page 264) and sulphonation followed by neutralization:



The resulting product is a mixture of sulphonates with alkyl groups of differing length. Moreover, because of the isomerizing effect of AlCl_3 , the alkylation results in the formation of a mixture of compounds, in which the phenylsulphonate group is linked to various secondary carbon atoms of the alkyl groups.

Alkyl aryl sulphonates are crystalline solids. When the alkyl chain is branched, alkyl aryl sulphonates dissolve well in water; with straight and longer alkyl chains the solubility in water and alcohols decreases. These sulphonates are colourless and odourless (the odour is present only in some products that have not been separated completely from kerosene fractions). They are used in the production of detergent compositions intended for the laundering of clothes and fabrics, for dishwashing, for the washing of various packages and wool, for bleaching of chemical fibres, etc.

The sulphonation step in the production of these surfactants has been for a long time effected using oleum alone—either batchwise or continuously according to the flow diagram given in Fig. 5.5. The sulpho mass contained sulphuric acid; it was separated by diluting the mass with water until 60-70 percent H_2SO_4 (in which the alkyl-arylsulphonic acid is insoluble) was obtained.

The most promising methods today are those based on the use of SO_3 . The flow diagram for the sulphonation with SO_3 vapours diluted with air does not differ from that employed for the sulphation of alcohols. A partial flow diagram for the sulphonation by SO_3 in a

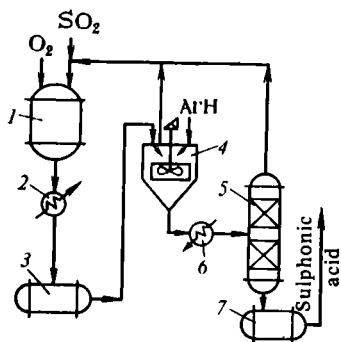


Fig. 5.6. Flow diagram of sulphonation in a solution of liquid sulphur dioxide:

1—unit for oxidation of SO_2 to SO_3 ;
2—cooler; 3, 7—collectors; 4—reactor;
5—vaporizer; 6—heater.

solution of sulphur dioxide is presented in Fig. 5.6. This production is usually combined with the partial oxidation of SO_2 to SO_3 by technical oxygen in unit 1. The products are cooled and condensed in cooler 2 and then collected in collector 3 in the form of 10-15 percent solution of SO_3 in liquid SO_2 . This solution and also the solution of an alkyl-aromatic hydrocarbon in liquid SO_2 are introduced into the tray of reactor 4; it overflows onto the wall and there the reaction is completed in the dripping film. The liquid leaving the reactor still contains 5-7 percent of SO_2 ; in order to remove SO_2 ,

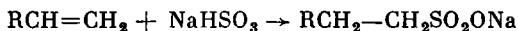
the liquid is heated and sent to vacuum vaporizer 5, after which it overflows into collector 7 and is then passed for further processing steps (neutralization, mixing, drying, packing), which are carried out according to the scheme shown in Fig. 5.3. The gaseous SO_2 from the top of the reactor and vaporizer is returned to unit 1.

5.3. Sulphochlorination and Sulphoxidation of Paraffins. Surfactants of the Alkyl Sulphonate Type

Sulphuric acid and its derivatives do not react with paraffins, in contrast to olefins and aromatic compounds. Therefore, alkylsulphonic acids and their salts were produced by using other reactions, say the reaction of alkyl chlorides with sodium sulphite:



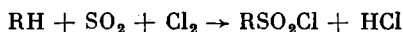
the radical-chain addition of sodium bisulphite to olefins



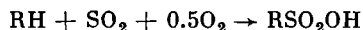
the oxidation of mercaptans.

Two important reactions of saturated hydrocarbons were discovered in the late thirties—sulphochlorination and sulphoxidation, which have become as important for this class of hydrocarbons as the action of sulphuric acid and its derivatives on aromatic compounds.

Sulphochlorination consists of the reaction of sulphur dioxide and chlorine with a paraffinic hydrocarbon upon illumination:



Upon irradiation or in the presence of initiators of radical-chain reaction sulphur dioxide and oxygen react with paraffins to give sulphonic acids (the *sulphoxidation* reaction):

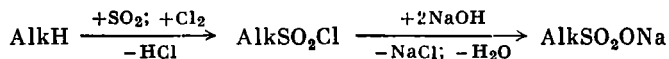


These processes have made it possible to produce sulphonic acids of the aliphatic series by way of replacement of hydrogen atoms in paraffinic hydrocarbons.

Detergents are made through the neutralization of the sulphochloride and sulfoxide, respectively, with caustic. The resultant alkyl sulphonates are inferior to alkyl sulphates and sulphonols with respect to surface-active and detergent properties, especially in hard water. The nearer is the sulphonate group to the end of the carbon chain, the better are the properties of the product. Maximum surface activity is exhibited by sulphonates having a straight chain of 14-16 carbon atoms, a circumstance that dictates the choice of the feedstock (the kerosene fraction of paraffin-base petroleum or soft paraffin wax produced with the aid of molecular sieves or carbamide). Because of the stickiness and low crystallinity, alkyl sulphonates are mainly used in the form of solutions as emulsifiers, subsidiaries, liquid soaps and additives to other detergents.

5.3.1. Sulphochlorination of Paraffins

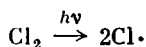
The sulphochlorination reaction, which was discovered by Read and Hopf in 1936, is employed for the production of surface-active agents of the type of alkyl sulphonates. For this purpose, sulphochlorides are converted by the action of caustic to salts of sulphonic acids:



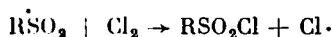
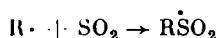
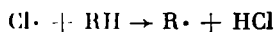
Aliphatic sulphochlorides, which are highly reactive compounds, are suited for the synthesis of a number of valuable products. They react with alcohols, phenols, amines and give esters and amides ($\text{RSO}_2\text{OR}'$, $\text{RSO}_2\text{NHR}'$), which find application as plasticizers,

intermediates, etc. The sulphochlorination of polyethylene gives a rubber-like polymer readily vulcanizable by diamines.

Basic Regularities of the Reaction. Sulphochlorination is a strongly exothermic and irreversible process; it is effected by bubbling gaseous sulphur dioxide and chlorine through the reagent upon irradiation with ultraviolet light. Just as in the chlorination of paraffinic hydrocarbons, the chain initiation occurs due to the homolytic cleavage of the chlorine molecule upon absorption of a light quantum:



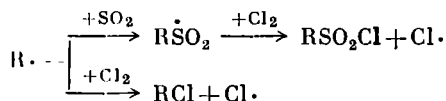
The chain step consists of the following sequence of conversions:



According to the available data, the quantum yield reaches 2000.

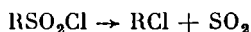
In order to avoid the inhibition of the reaction by oxygen, the sulphochlorination reaction must be carried out using the gas obtained by the evaporation of liquid chlorine. Moreover, there are additional requirements to the quality of the organic feedstock: it must not contain sulphur compounds and other impurities that exert an inhibiting action.

One of the side reactions involved in the sulphochlorination is the parallel photochemical chlorination of the reagents leading to the formation of chloro derivatives:



Obviously, the suppression of chlorination is favoured by an excess of sulphur dioxide with respect to chlorine. In the case of straight-chain hydrocarbons even at a molar SO_2/Cl_2 ratio of 1.1:1 the fraction of the chlorination reaction is 3-5 percent, which is quite suitable for industrial practice. Olefins and aromatic hydrocarbons are predominantly chlorinated upon sulphochlorination. Therefore, no impurities of these compounds must be present in the feedstock, which is why the feedstock must be subjected to purification.

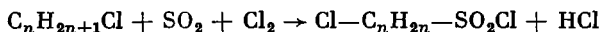
A certain amount of chloro derivatives results also from the desulphonation of sulphochlorides with liberation of sulphur dioxide:



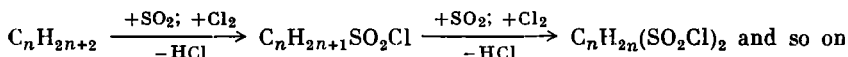
This decomposition is favoured by elevated temperature, which is why the temperature range is limited to 30-35 °C.

The relative reactivity of various hydrogen atoms on sulphochlorination is different from that in chlorination reactions, probably because of steric hindrances upon approach of the sulphur dioxide molecule to a tertiary alkyl radical: secondary > primary > tertiary. As a result, in the sulphochlorination of isoparaffins the fraction of the side chlorination reaction is considerably increased. With normal C₁₂-C₁₈ paraffins, secondary sulphochlorides are predominantly formed, in which the sulphonic acid group is located at any of the secondary carbon atoms.

The resulting chloro derivatives may also undergo sulphochlorination. As a result, the sulphochlorination of hydrocarbons, especially when they are recycled upon gradual accumulation of chloro derivatives leads to the formation of by-product chlorosulphochlorides:



Like the chlorination of paraffinic hydrocarbons, sulphochlorination belongs to the class of consecutive-parallel processes. The initially formed monosulphochloride is subjected to further substitution, which gives a disulphochloride, etc.:



The second step proceeds more slowly than the first because the sulphochloride group lowers the ability to undergo further substitution. As a result, the maximum content of monosulphochloride in the reaction mass is rather high, amounting to 50 percent (molar). Here, the composition of the products depends, just as in other analogous cases, on the ratio of the reagents, i.e., on the ratio of SO₂ (or Cl₂) to RH, or, in other words, on the relative number of sulphochloride groups and starting hydrocarbon molecules in the reaction mass. Hence, in order to obtain monosulphochloride, an excess of the hydrocarbon is required, and only a limited amount of sulphochlorides accumulated in the reaction mass is permissible. The unreacted hydrocarbon is separated from the reaction products and recycled to sulphochlorination. The need for this operation is dictated by the low surface activity of disulphonates and by the saving of the feedstock. In industrial practice, the reaction is most often conducted until there is accumulated 30 percent (by weight) of sulphochlorides with recycle of 70 percent (by weight) of the neutral oil. The resulting sulphochlorides contain about 94 percent (by weight) of mono- and 6 percent (by weight) of disubstituted compounds.

Technology of Production of Alkyl Sulphonates. The technology of the sulphochlorination process is similar in many respect to the liquid-phase radical-chain chlorination of paraffins (page 117). The process is effected mainly photochemically in column reactors

fitted along its height with devices for irradiation of the mixture by means of mercury-quartz lamps. The radiochemical method using γ -radiation from a ^{60}Co source is used. The continuous process often employs a single bubbler column, though the composition of the reaction mixture is impaired somewhat in such an apparatus because of back-mixing during the bubbling of the gas. It has been suggested that the process be conducted in a cascade of bubbler units or in a sectional column with trays.

The flow diagram of the production of alkyl sulphonates by photochemical sulphochlorination is shown in Fig. 5.7. The chlorine

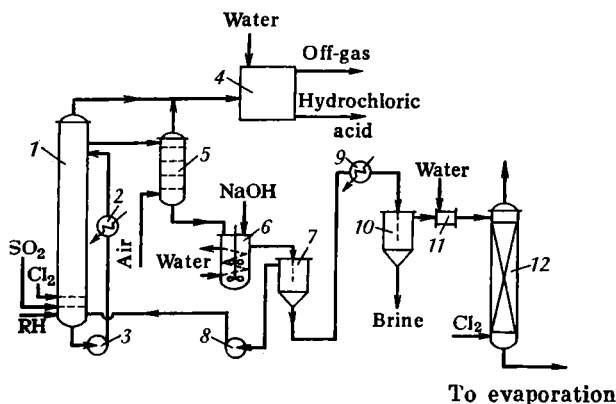


Fig. 5.7. Flow diagram of production of alkyl sulphonates by photochemical sulphochlorination:

1—sulphochlorinator; 2, 9—coolers; 3, 8—pumps; 4—unit for recovery of HCl and purification of the off-gases; 5—air blower; 6—neutralization unit; 7, 10—separators; 11—mixer; 12—bleaching column.

obtained by the evaporation of liquid chlorine and the gaseous SO_2 in 5-percent excess are introduced into the bottom of sulphochlorinator 1 through distributing pipes; they bubble through the liquid layer that fills the column. A fresh paraffinic fraction and the unconverted hydrocarbon separated from the product are also led into sulphochlorinator 1. The heat of the reaction is removed in an external cooler 2, through which the reaction mixture is pumped. The gases leaving the column consists of HCl and unconverted SO_2 . These are passed to purification unit 4 of the same type as in chlorination processes; in this unit, HCl is absorbed by water to give concentrated hydrochloric acid and then the gas is purified from toxic substances in a caustic scrubber.

The resultant mixture is passed from the sulphochlorinator through the side overflow pipe to blower 5, where the dissolved HCl and SO_2 are removed from it by an air current. The mixture is then neutralized with aqueous caustic at $\approx 100^\circ\text{C}$ in neutralizer 6 and decanted in

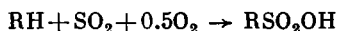
separator 7. The upper layer contains unconverted hydrocarbons and a small amount of chloroalkanes, which are returned to sulphochlorination by pump 8.

The aqueous solution accumulated in the lower part of separator 7 is cooled in cooler 9 down to 5-10 °C and allowed to settle in separator 10. At the temperature indicated and with a certain amount of water present in the mixture there occurs "desalting" of alkyl sulphonates from the solution, and they are collected at the top in the form of a paste. The lower layer of the aqueous solution of sodium chloride (brine) still contains up to 20 percent of alkyl sulphonates which have to be extracted by alcohol.

The paste of alkyl sulphonates from separator 10 is diluted with water to a 20-percent concentration in mixer 11 and bleached in column 12. The solution is then led for vacuum stripping, which yields the commercial product in the form of a 50-60 percent aqueous solution of alkyl sulphonates.

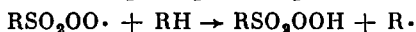
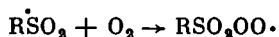
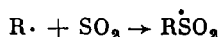
5.3.2. Sulphoxidation of Paraffins

Basic Regularities of Sulphoxidation. The sulphoxidation reaction, which was discovered by Platz in 1940, proceeds according to the equation

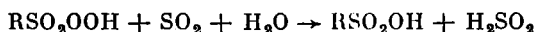


and is irreversible and strongly exothermic. It is accelerated by illumination or by the action of initiators of radical-chain reactions, which clearly points to its free-radical mechanism. In this respect, there are observed many similarities with sulphochlorination and oxidation reactions.

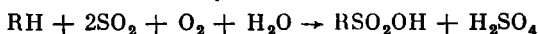
The free radical formed as a result of chain initiation starts a chain of conversions involving the following elementary steps:



This involves the intermediate formation of the sulphoperoxide radical and a sulphohydroperoxide. The latter is sufficiently stable at the reaction temperature and is the end product if no foreign compounds are introduced. When water is introduced into the reaction mixture (*the water-light method*), the sulphohydroperoxide oxidizes SO_2 to sulphuric acid, being itself converted to a sulphonic acid:

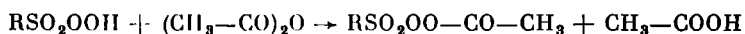


Thus, the overall reaction equation is as follows:

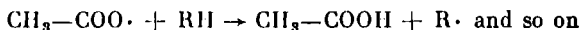
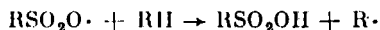
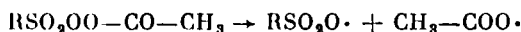


The reaction with higher paraffins differs by a small chain length (5-10) from sulphochlorination, in which the chain length amounts to several thousands. This requires considerable expenditure on irradiation.

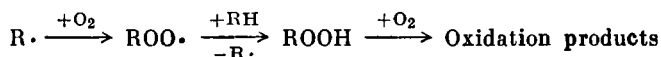
Another method of accomplishing the sulphoxidation has been developed with a view to reducing the consumption of sulphur dioxide and using peroxide compounds for the initiation of the reaction. The entire process splits into two steps. In the first step, the sulphoxidation is conducted under illumination in an anhydrous medium but in the presence of acetic anhydride, which binds the sulphohydroperoxide into acetylsulphoperoxide, which is stable towards decomposition:



The second step proceeds in the dark and at a higher temperature, at which acetylsulphoperoxide becomes capable of initiating a radical-chain sulphoxidation process:



With any of the methods described above there occurs a side oxidation reaction because the free radical can react not only with sulphur dioxide but also with oxygen:



The extent of the side oxidation reaction is insignificant for straight-chain hydrocarbons, but it increases with isoparaffins and aromatic compounds having side chains. This is accounted for by the fact that the reactivity of various hydrogen atoms upon sulphoxidation varies in the same way as with sulphochlorination: secondary > primary > tertiary, and the oxidation, on the contrary, proceeds most rapidly at the tertiary carbon atom. Therefore, isoparaffins and also olefins and aromatic hydrocarbons prevent sulphoxidation. With *n*-paraffins in the C₁₂–C₁₈ range, just as in the case of sulphochlorination, there is formed a mixture with an equally probable location of the sulphonie-acid group at all secondary carbon atoms.

Technology of Sulphoxidation Processes. In the water-light method, the process is carried out in one step at 25-30 °C by continuously irradiating the reaction mass with ultraviolet light and by extracting sulphuric and sulphonic acids by water. The reactor is a hollow column fitted with illumination devices and external coolers. Sulphur dioxide and oxygen are introduced into the bottom of the reactor through a bubbler column, and the feedstock and water are con-

tinuously supplied into the upper part of the reactor. The emulsion is separated into two layers in the separator, from which the hydrocarbon is again led to the reaction and the aqueous solution of sulphuric and sulphonc acids is sent for further processing. The C_{12} - C_{20} sulphonc acids do not dissolve in the aqueous solution of sulphuric acid and can be separated by decantation. The liquid sulphonc acids are then led to neutralization and the aqueous solution of their salts is evaporated until about a 50-percent paste-like mixture of alkyl sulphonate and water is obtained.

In the two-step process involving acetic anhydride, the reaction is carried out in two different units. In the first reactor, photochemical initiation is effected, acetic anhydride being introduced into the reaction mass and a temperature of 40 °C is maintained, at which acetylsulphoperoxide is formed. The second stage is accomplished at 60 °C in the second apparatus, into which the reaction mass from the first reactor and a mixture of sulphur dioxide with oxygen are introduced.

Both methods of producing alkyl sulphonates (by sulphochlorination and sulphoxidation) have advantages and shortcomings. The first method employs a large amount of caustic and chlorine, which are lost in the form of wastes which are difficult to use. In this respect, sulphoxidation is more favourable, but the shortcomings of this process are the consumption of a large amount of sulphur dioxide and the formation of by-product sulphuric acid; the two-step process requires an additional quantity of acetic anhydride (≈ 90 kg per 1 ton of sulphonate). The scope of industrial application of the two processes (sulphochlorination and sulphoxidation) is the same. Because of the shortcomings indicated above and of the lowered detergent properties of the alkyl sulphonates produced both methods are of relatively little value; only 3-5 percent of the total production of anionic surfactants is produced by these processes.

5.4. Nitration Processes

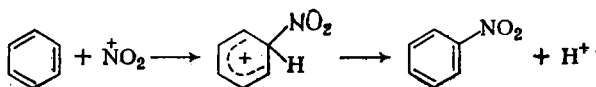
The nitro group can be introduced into organic compounds by various methods, the choice of which depends on the class of starting hydrocarbons. The following two processes are of prime industrial importance: (1) nitration into the aromatic ring (nuclear nitration); and (2) nitration of saturated hydrocarbons.

5.4.1. Nitration of Aromatic Compounds

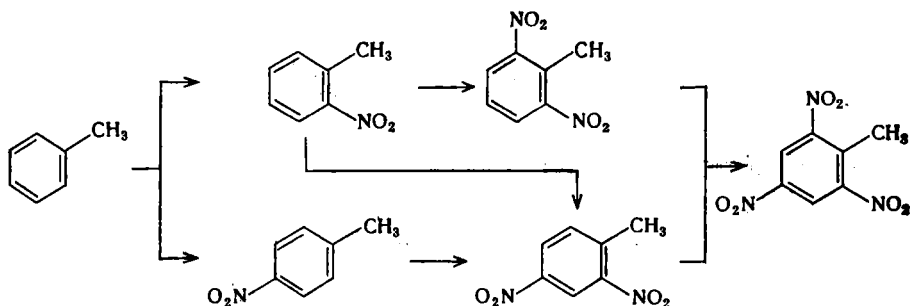
The nitration of aromatics is most often effected with a mixture of nitric and sulphuric acids. Sulphuric acid is simultaneously used as a catalyst, a dehydrating agent and also as a substance contributing to a more complete use of nitric acid and preventing oxidation

processes. The nitrating mixture undergoes an acid-base interaction leading to the formation of a very active nitrating agent—the nitronium ion NO_2^+ :

$\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O}-\text{NO}_2 + ^-\text{OSO}_2\text{OH} \rightleftharpoons \text{NO}_2^+ + \text{HOSO}_2\text{O}^- + \text{H}_2\text{O}$
which attacks the aromatic ring:



The effect of substituents on the reactivity of the aromatic ring and on the orientation of the entering nitro group is the same as in other electrophilic substitution reactions in the aromatic ring. Because of the strong deactivating effect of the nitro group, each of the subsequent steps of nitration occurs much more slowly than the preceding one $[(k_n/k_{n-1}) \ll 1]$. Therefore, the reaction can be accomplished with high yield of any of the products of the consecutive-parallel substitution (mono-, di- or trinitro derivatives) by choosing a nitrating agent of suitable strength and a suitable temperature. For example, the nitration of toluene carried out initially under mild conditions (40°C) yields mononitrotoluenes (a mixture of 58-59 percent of *ortho*-, 4-5 percent of *meta*- and 36-39 percent of *para*-isomer), which under more severe conditions ($70-80^\circ\text{C}$) give dinitrotoluenes (a mixture of mainly 2,4- and 2,6-isomers), and finally trinitrotoluene is produced:



The reaction conditions, which are mainly determined by the temperature of the process and by the nitrating power of the sulphuric acid-nitric acid mixture, depend on the reactivity of the aromatic compound. The nitrating power of the starting acid mixture is determined by the concentrations of sulphuric acid, $C_{\text{H}_2\text{SO}_4}$, and of nitric acid, C_{HNO_3} , and water in the mixture. The nitrating ability of the starting acid mixture can be estimated by using the nitrating activity

factor (NAF):

$$\text{NAF} = C_{\text{H}_2\text{SO}_4} \frac{140}{140 - C_{\text{HNO}_3}}$$

In this formula, the fraction characterizes the dilution of the acid by the water formed; it is equal to

$$\frac{140}{140 - C_{\text{HNO}_3}} = \frac{100}{100 - C_{\text{HNO}_3} + \frac{18}{63} C_{\text{HNO}_3}} = \frac{100}{100 - 0.714 C_{\text{HNO}_3}}$$

where 18 and 63 are the molecular masses of water and nitric acid. Hence, the NAF is numerically equal to the concentration of spent H_2SO_4 provided that HNO_3 is used completely. For the nitration of each aromatic compound there is a specific limiting value of NAF, which is the higher, the lower is the reactivity of the compound (compare with the sulphonation π -factor; page 357). In practice, some excess of HNO_3 is taken, this being dictated by the desire to intensify the process and to effect the complete conversion of the aromatic compound. Naturally, the extent to which nitric acid is used in such a case is lower than 100 percent. For instance, in the preceding example of the nitration of toluene, the NAF must be equal to 70 in the first step and 82 in the second; it may even amount to 93 for further conversion to trinitrotoluene. Under the conditions indicated, the extent of utilization of nitric acid amounts, respectively, to 96, 90 and 50-60 percent. Analogously, benzene is nitrated successively to nitrobenzene (NAF = 70; 65-70 °C), which is then converted to *m*-dinitrobenzene (NAF = 88; 80-90 °C).

The nitration of aromatic compounds is an irreversible and highly exothermic reaction (≈ 151 kJ/mol or 36 kcal/mol per nitro group). Just as with sulphonation, the heat effect increases because of the dilution of the nitrating mixture by the liberated water and varies, depending on the concentration of sulphuric acid.

In the nitration of hydrocarbons or chloro derivatives, the reaction mass consists of two immiscible liquids. In order to avoid local overheating and side oxidation reactions, intensive stirring and cooling are required, which simultaneously contribute to the acceleration of the process. It is usually carried out in a cascade of stirred reactors; each reactor is followed by a separator for the separation of the organic phase from the nitrating mixture. The fresh nitrating mixture (or hydrocarbon) is introduced into the last reactor, where the most forcing conditions are required for the exhaustive nitration of the starting compound. The spent acids from this reactor are separated and sent to the preceding reactor, and so on; in this way the countercurrent flow of the nitrating mixture and the organic reagent is effected (Fig. 5.8).

Aromatic nitro compounds play an important role as explosives and intermediates mainly in the production of amines (aniline from nitrobenzene, toluidines from mononitrotoluene, *m*-phenylenediamine and *m*-toluylenediamine from dinitrobenzene and dinitrotoluene).

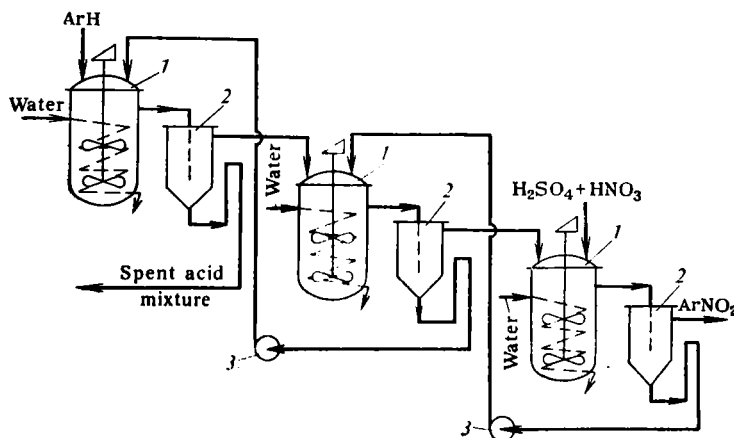
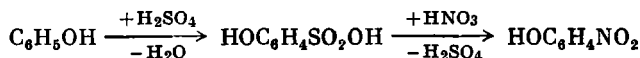


Fig. 5.8. Reaction unit for nitration of aromatic compounds:
1—nitraters; 2—separators; 3—pumps.

Nitrophenols usually result from the sulphonation step (the phenols themselves are oxidized by nitric acid):



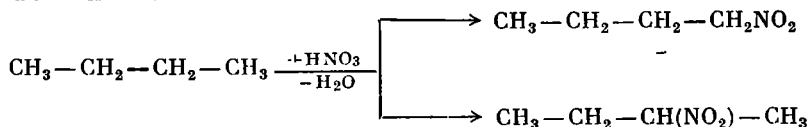
Nitrophenols are used for a number of syntheses, including the production of parathions possessing high insecticide activity. For instance, the organophosphoric preparations thiophos and métaphos encountered earlier contain a *p*-nitrophenoxy group.

5.4.2. Nitration of Saturated Hydrocarbons

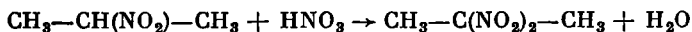
The nitration of paraffins was first accomplished by M.I. Kononov at the end of the 19th century. Later the following methods of nitration of paraffins were used on an industrial scale: (1) nitration in the vapour phase at 350–500 °C using 40–70-percent HNO_3 ; (2) nitration in the liquid phase at 100–200 °C using 50–70-percent HNO_3 ; (3) nitration in the liquid or vapour phase using nitrogen tetroxide (or dioxide).

In the nitration of paraffins, just as in processes of their chlorination, the nitro group enters any position in the starting hydrocarbon, replacing hydrogen atoms on various carbon atoms; just as in the

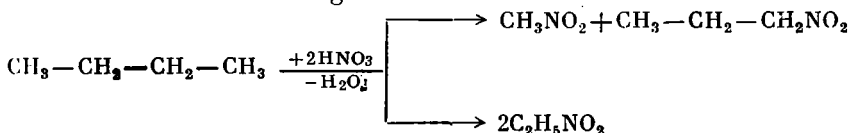
chlorination of paraffins, tertiary hydrogen atoms are most readily replaced, secondary react more sluggishly and primary hydrogen atoms are relatively unreactive. As the temperature is increased the reactivities come closer together, but in any case (where it is allowed by the structure of the starting hydrocarbon) there is formed a mixture of isomeric nitroparaffins, but no isomerization of the carbon skeleton occurs:



The nitro group prevents further substitution strongly, which is why the vapour-phase nitration, which is always carried out with an excess of hydrocarbon (from 3 : 1 to 10 : 1), gives no dinitro derivatives. However, in the liquid-phase nitration the mononitro compound dissolves in nitric acid much better than the starting hydrocarbon and dinitro derivatives are formed. The second nitro group enters either the positions remote from the first carbon atom or those at a carbon atom that already bears a nitro group. Hence, just as in chlorination, it is the hydrogen atoms on neighbouring carbon atoms that are mainly deactivated. By virtue of this, 2,2-dinitropropane can be obtained in good yield from 2-nitropropane:



The high-temperature vapour-phase nitration of paraffins always gives also lower nitroparaffins, which result from the fission of the carbon chain. Their composition corresponds to the cleavage of any C—C bond in the starting molecule:



This process may be called *destructive nitration*. For branched hydrocarbons it occurs to a lesser extent than for straight-chain paraffins, but lengthening of the chain results, other conditions being equal, in a stronger destruction than in nitration. For instance, the reactions of paraffins with nitric acid at 420 °C yield the following amount of lower nitroparaffins: 32 percent from *n*-butane, 42 percent from *n*-pentane, 38 percent from isopentane, and 27 percent from 2,2-dimethylpropane. As the temperature is lowered the fraction of destructive nitration is diminished. It is because of this that no lower nitroparaffins are formed, as a rule, in liquid-phase nitrations. For example, the nitration of propane by nitric acid gives the following total amounts of nitromethane and nitroethane (in percent of the

total amount of nitroparaffins): 35 percent at 430-450 °C, 39 percent at 505-510 °C and 57 percent at 590-595 °C.

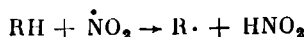
The main undesirable reaction in all nitration processes is the oxidation of paraffins by nitric acid or nitrogen dioxide. The yield based on nitric acid is therefore rather low, mostly 50-80 percent. The oxidation products have been found to contain aldehydes and ketones, carboxylic acids, carbon monoxide and dioxide, etc. On the other hand, because of the reduction of the nitrating agent there are formed lower oxides of nitrogen and even free nitrogen. In the nitration of cycloparaffins, say cyclohexane, the oxidation products formed include also dicarboxylic acids, namely adipic, glutaric and succinic acids, these being formed as a result of the oxidative degradation of the ring. The oxidative processes are enhanced with increasing temperature. Therefore, for each hydrocarbon there is an optimum nitration temperature, which gives a higher yield of nitro compounds. In nitrations with nitrogen dioxide this temperature is lower than with nitric acid.

A comparison of nitric acid with nitrogen dioxide as nitrating agents used at the corresponding optimum temperatures shows that with nitric acid the yield of nitroparaffins based on nitrogen and the formation of olefins, aldehydes and ketones are higher than with nitrogen tetroxide, and the yield of nitroparaffins based on the starting hydrocarbon and the formation of carbon monoxide are lower. When HNO_3 is used, the contact time required for a successful completion of the process is also reduced.

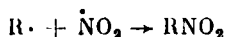
The nitration of paraffins belongs to the class of free-radical processes. Free radicals appear as a result of the homolytic cleavage of nitric acid and of the subsequent interaction of the particles formed with the hydrocarbon:



The nitrogen dioxide formed in the first reaction or the one used as the nitrating agent is also capable of reacting with the hydrocarbon and splitting off the hydrogen atom from it (this is accounted for by the structure of nitrogen dioxide, which has an unpaired electron):



The main nitration reaction proceeds by way of the interaction of free radicals with nitrogen dioxide:



which does not permit the chain process to be developed.

The processes of destructive nitration and oxidation occur due to the formation of nitrous acid according to the above-given equation

prevents the formation of explosive mixtures, overheatings, and excessive oxidation.

The heated propane is passed into the bottom of the reactor. The nitration and oxidation products together with the unreacted propane, which is taken in considerable excess, are cooled with water in cooler 3 and led to absorber 4 to recover the products of the oxidation (aldehydes and ketones) and condensation of nitro compounds. The absorber is refluxed with an aqueous hydroxylamine hydrochloride solution, which binds the volatile carbonyl compounds into

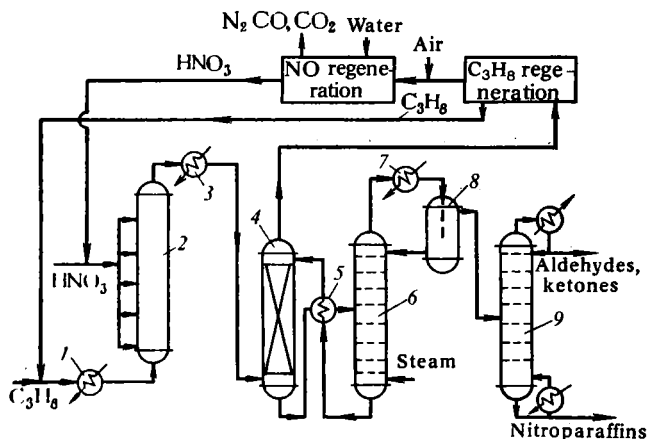


Fig. 5.9. Flow diagram of nitration of propane:

1—heater; 2—reactor; 3—cooler; 4—absorber; 5—heat exchanger; 6—stripping column; 7—condenser; 8—separator; 9—fractionating column.

oximes. The liquid from the still of the absorber is run to stripping column 6, where the nitroparaffins and also the aldehydes and ketones resulting from the hydrolysis of oximes, are distilled off from the absorbent, which is cooled in cooler 5 and returned to the absorber. The vapours from stripping column 6 are condensed in cooler-condenser 7 and separated into two layers in separator 8. The lower, aqueous layer is returned to the top tray of the stripping column and the upper, organic layer is led to fractionating column 9. In this column, the highly volatile aldehydes and ketones distill off and the mixture of nitroparaffins is collected in the still of the column. The nitroparaffins are sent for further processing, which consists of their purification and fractionation, in which the water, nitromethane, nitroethane, 2-nitropropane and 1-nitropropane are successively distilled off.

The economy of the process depends to a considerable extent on the possibility of recovery of propane and oxides of nitrogen present in the gases leaving the absorber. These gases contain ≈ 85 percent

of C_3H_8 and 10 percent of NO . In the recovery system, propane is isolated from the mixture by compression and cooling or absorption using kerosene, in which the other constituents (N_2 , CO , CO_2) are insoluble. To the gas left is added air, and the nitrogen dioxide formed is recovered by water or dilute nitric acid. Here the oxides of nitrogen are converted to nitric acid and the remaining gas is discharged to the atmosphere. The recovered propane and nitric acid are mixed with fresh reagents and recycled to the nitrator.

The production of nitroparaffins by the method described presents explosion hazard. Besides, the apparatus is exposed to the action of strongly corrosive nitric acid at a high temperature, which is why the reactor is constructed of alloy steel, ferrosilicon, titanium and tantalum (the last is resistant to the action of nitric acid under any conditions).

The most efficient method of liquid-phase nitration of paraffins ($>C_{10}$) boiling higher than $160-180^\circ C$ is the nitration with vapours of nitric acid. In this case, the liquid hydrocarbon in the reactor of the bubbler type is nitrated at $130-220^\circ C$. The liquid acid is continuously fed into the coil immersed in the reaction mass. Upon heating and vaporization the acid absorbs the heat evolved during the reaction. The vapours of the acid are then passed into a distributing unit and are bubbled through the reaction mass, thereby effecting the nitration of the hydrocarbon. An advantage of this method is the presence of only a small amount of vapours of nitric acid in the reaction space, which is why the process presents no explosion hazard and is easily controlled.

The nitration of lower-boiling hydrocarbons (C_6-C_9) is accomplished by two liquid-phase methods if they give many cracked products in the vapour phase. These two methods are associated with the use of elevated pressure (0.2-1 MPa) required for maintaining the reaction mass in the liquid state. In one of these methods, the reaction is effected using liquid nitrogen tetroxide, which is capable, in contrast to nitric acid, of dissolving in hydrocarbons. The mixture is passed through a cooled tubular reactor at $170-180^\circ C$ and a contact time of several minutes. In the other method, the nitration is carried out with 50-70-percent nitric acid at $120-180^\circ C$. Because of the high exothermicity of the process and of the heterogeneous nature of the reaction mass, which contribute to local overheatings, it is necessary that the liquid be stirred intensively or circulated and cooled. The process is speeded up by addition of nitrogen dioxide, which properly plays the role of the initiator that generates free radicals.

The liquid-phase nitration of 2-nitropropane gives 2,2-dinitropropane, which is used as an additive to diesel fuels to raise the cetane number. The liquid-phase nitration of cyclohexane to nitrocyclohexane forms the basis for one of the possible methods of producing caprolactam (see Chapter 9).

CHAPTER 6

OXIDATION PROCESSES

The practical importance of oxidation processes in the industry of basic organic and petrochemical synthesis is difficult to overestimate. They have become of prime importance due to the following factors.

1. The great value of compounds obtained by oxidation (alcohols, aldehydes, ketones, carboxylic acids and their anhydrides, α -oxides, nitriles, etc.) and used as intermediates in organic synthesis, solvents, monomers and as the feedstock for the production of polymeric materials, plasticizers, etc.

2. The wide range of various oxidation reactions in which many organic compounds, including all classes of hydrocarbons, can participate. This makes it possible to use oxidation processes for the primary processing of the hydrocarbon feedstock and to produce a large number of valuable compounds.

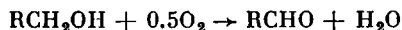
3. The availability and low cost of most oxidizing agents, the most important of which is the air oxygen. This makes the synthesis of some products by oxidation methods highly economical as compared with other possible methods of their manufacture.

The factors just described have been responsible for the extensive application of oxidative processes in organic synthesis, and these processes often replace other, less economical methods of manufacture of many products. The scale of application of these processes is also large, which can be seen from the following data on the annual production of some compounds in the USA (the forecast for 1980, in million tons):

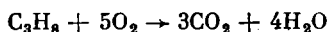
Ethylene oxide	2.3
Phenol	1.2
Acetone	1.1
Acetic acid	1.1
Vinyl acetate	0.8
Acetaldehyde	0.7
Phthalic anhydride	0.55

6.1. General Description of Oxidation Processes

Definition and Classification of Oxidation Processes. In organic chemistry it is no simple matter to define oxidation reactions. In contrast to inorganic chemistry, oxidation reactions in organic chemistry are not usually accompanied by a change in the valency of atoms. Nor is the introduction of oxygen atoms into the molecule a feature specific to all oxidation reactions: this also occurs in other reactions (hydrolysis, hydration) which bear no relation to oxidation reactions; moreover, there are oxidation reactions in which the number of oxygen atoms in the molecule is not changed; an example is the following reaction:

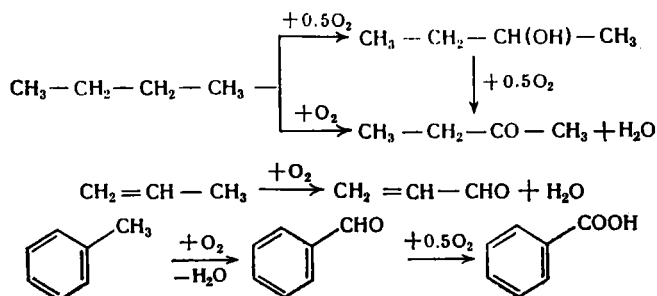


Thus, in organic chemistry and technology, oxidation processes are defined as conversions of compounds under the influence of various oxidizing agents. A distinction is made between complete and partial oxidation. By complete oxidation is meant the combustion of substances with the formation of carbon dioxide, water, etc.:

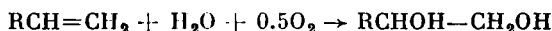
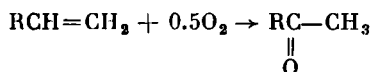
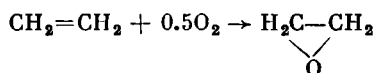


In organic synthesis, complete oxidation is an undesirable side process. It is partial oxidation which is important for organic synthesis; partial oxidation reactions may be divided into three main groups:

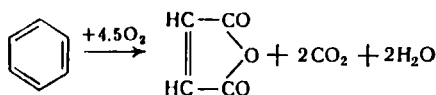
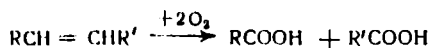
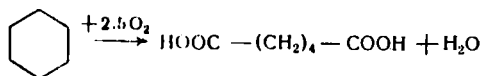
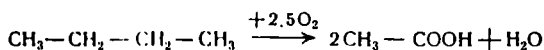
1. Oxidation without rupture of the carbon chain, when the number of carbon atoms remains the same as in the starting compound. These reactions may in turn be subdivided into two groups: oxidation across the saturated carbon atoms in paraffins, naphthenes, olefins and alkylaromatic hydrocarbons and in the derivatives of these compounds, especially in alcohols and aldehydes:



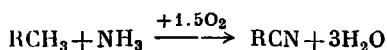
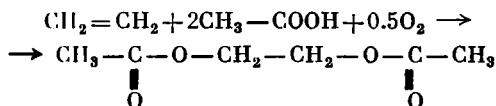
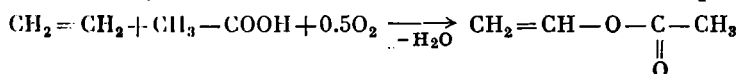
and oxidation at the double bond with the formation of α -oxides (*epoxidation*), carbonyl compounds or glycols:



2. Destructive oxidation which proceeds with the scission of carbon-carbon bonds. This oxidation reaction is exhibited by hydrocarbons (and their derivatives) of the paraffinic, naphthenic and olefinic series and also aromatic hydrocarbons. The disruption occurs at a single, double or aromatic bond:



3. Oxidation accompanied by the combination of the molecules of the reactants (oxidative condensation or oxidative coupling):



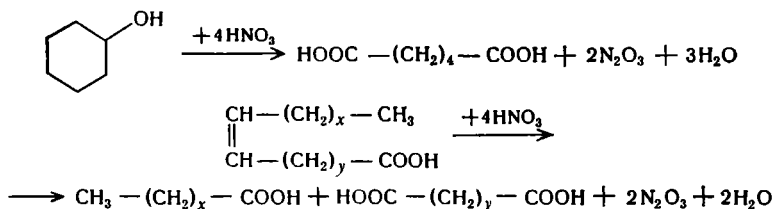
The last reaction is known as *oxidative ammonolysis* (or *ammozidation*).

Oxidizing Agents and Safety in Oxidation Processes. In laboratory practice and in fine organic synthesis use is not infrequently made of oxidizing agents, such as permanganates (in an alkaline, neutral or acidic medium), bichromates, chromium trioxide, pero-

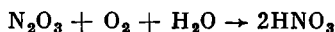
xides of some metals (manganese, lead, sodium), but in the industry of basic organic and petrochemical synthesis the tendency is to use cheaper oxidizing agents and only in some isolated cases, where such agents do fail to effect the reaction, are other oxidizing agents resorted to.

Molecular oxygen (in the form of air, technical oxygen or even nitrogen-oxygen mixtures with a small amount of O_2) is one of the most important oxidizing agents. It is used to carry out most of the oxidation reactions listed above. Concentrated oxygen exerts a stronger oxidizing action, but its use is associated with extra expenditure on the separation of air. When oxidation is carried out in the vapour phase, in which case the nitrogen impurity complicates the recovery of the products or their recycling, use is made of technical oxygen. The lower rate of the reaction on oxidation by air is compensated for by an increase in temperature or an increase in the total pressure, which leads to an increase in the partial oxygen pressure.

Nitric acid (less frequently, oxides of nitrogen) ranks second as an oxidizing agent after molecular oxygen in scope of application. Its action is not infrequently accompanied by the side nitration of an organic compound, which is enhanced with increasing concentration of the acid. It is for this reason that 40-60-percent HNO_3 is used for oxidation. Nitric acid has never been used as an oxidizing agent for reactions with paraffins. Typical reactions for nitric acid are disruptive oxidations of cyclic compounds and compounds having unsaturated bonds, which give a higher yield with HNO_3 than with oxygen:

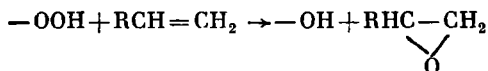


When nitric acid is used for oxidation, it is reduced to nitrogen oxides (NO or N_2O_3). The cost of a manufacturing process is mainly dependent on the possibility of utilization of these oxides and of recovery of unconverted nitric acid. The first task is solved by the oxidation of nitrogen oxides by air in an aqueous or nitric-acid solution with the formation of nitric acid:

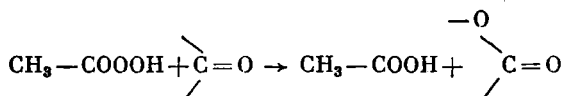


Peroxide compounds, primarily hydrogen peroxide and peracetic acid have found application as oxidizing agents relatively recently in basic organic and petrochemical synthesis (hydroperoxides have

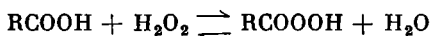
also lately been added to this group). Because of the relatively high cost, they are used only for reactions that do not proceed under the influence of molecular oxygen or nitric acid. This refers mainly to the epoxidation of unsaturated compounds:



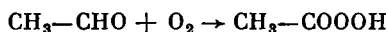
Of less importance is the reaction of peracids with ketones which yields esters or lactones (the Baeyer-Villiger oxidation):



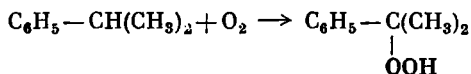
Hydrogen peroxide is usually employed in the form of a 30-percent aqueous solution. It reacts with carboxylic acids to give the corresponding peracids according to a reaction equation analogous to esterification:



Peracids are also formed upon oxidation of aldehydes. For example, *peracetic acid* is produced in this way on an industrial scale:

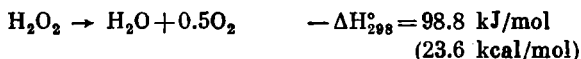


Hydroperoxides are produced commercially by the oxidation of hydrocarbons:



Safety in oxidation processes is necessary mainly because some oxidizing agents form explosive mixtures with organic compounds and others are compounds capable of decomposition. The explosive properties of gaseous mixtures of hydrocarbons with air and the flash points of liquid hydrocarbons have been described in Chapter 1. Other organic compounds (alcohols, ketones and aldehydes) are close to them with respect to explosive concentration limits; these limits become wider when use is made of pure oxygen. In liquid-phase oxidation reactions the explosion hazard is the greater, the higher is the vapour pressure of an organic compound that forms explosive mixtures with air or oxygen.

Nitric acid and other oxidizing agents also give explosive mixtures with organic substances. The danger from the presence of hydrogen peroxide and peracetic acid is enhanced by the fact that their decomposition reactions involving the liberation of water and acetic acid, respectively, are exothermic:

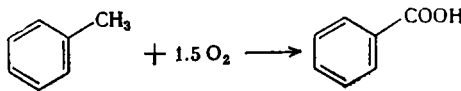
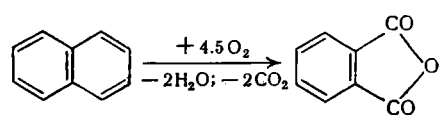


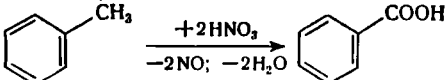
The decomposition of the peroxide compounds indicated is catalyzed by some metals of variable valency (Fe, Cu, Mn, Co, Cr) and their salts. Therefore, concentrated hydrogen peroxide and especially peracids are capable of explosion in the absence of organic compounds, which also refers to other peroxides. The use of these compounds in solutions and under controlled temperature conditions makes it possible to avoid these difficulties.

The risk of explosion of oxidizing agents and their mixtures with organic compounds is a very important factor which must be taken into account in the development and realization of technological oxidation processes.

Energy Characterization of Oxidation Reactions. All oxidation reactions that have found application in the industry of basic organic and petrochemical synthesis are irreversible. This does not mean that they cannot be effected at all in the reverse direction (for example, acids can be reduced to aldehydes and carbonyl compounds to alcohols and hydrocarbons), but for the reverse reaction to be accomplished, reducing agents or hydrogen are required. Hence, the oxidation is practically irreversible since its end products—carbon dioxide and water—cannot function as reducing agents.

Oxidation belongs to the category of the most exothermic processes of organic synthesis. The heat effects of the most popular oxidation reactions are given below (provided that all compounds are in the vapour phase):

Reaction	$-\Delta H_{298}^0$	
	kJ/mol	kcal/mol
(1) $\text{RCH}_2\text{R} + 0.5\text{O}_2 \rightarrow \text{RCH}(\text{OH})\text{R}$	146-188	35-45
(2) $\text{RCH}_2\text{R} + \text{O}_2 \rightarrow \text{RCOR} + \text{H}_2\text{O}$	ca. 355	ca. 85
(3) $\text{RCH}_3 + \text{H}_2 \rightarrow \text{RCHO} + \text{H}_2\text{O}$	284-336	68-80
(4) 	567.4	135.7
(5) $\text{RCHO} + 0.5\text{O}_2 \rightarrow \text{RCOOH}$	260-271	62-65
(6) $\text{RCH}_2\text{—CH}_2\text{R} + 2.5\text{O}_2 \rightarrow 2\text{RCOOH} + \text{H}_2\text{O}$	982-1003	235-240
(7) 	1807	432
(8) $\text{CH}_2=\text{CH}_2 + 0.5\text{O}_2 \rightarrow \text{CH}_3\text{—CHO}$	218.2	52.2
(9) $\text{CH}_2=\text{CH}_2 + 0.5\text{O}_2 \rightarrow \text{H}_3\text{C—CH}_2$ 	103.3	24.7

Reaction		$-\Delta H_{298}^{\circ}$	
		kJ/mol	kcal/mol
(10)	$\text{RCH}=\text{CH}_2 + \text{H}_2\text{O}_2 \rightarrow \text{RHC}-\underset{\text{O}}{\text{CH}_2} + \text{H}_2\text{O} \dots \dots \dots$	ca. 210	ca. 50
(11)	$\text{RCH}=\text{CH}_2 + \text{CH}_3-\text{COOOH} \rightarrow \text{RHC}-\underset{\text{O}}{\text{CH}_2} + \text{CH}_3-\text{COOH} \dots \dots \dots$	ca. 210	ca. 50
(12)		361	86.5

As can be seen from these data, the heat effect increases with increasing extent of oxidation, especially in the formation of carboxylic acids from hydrocarbons (reaction 4) and in the destructive oxidation of paraffins (reaction 6) and aromatic systems (reaction 7). The processes of formation of carbonyl compounds from hydrocarbons (reactions 2, 3 and 8) and carboxylic acids from aldehydes (reaction 5) are less exothermic. The heat effect decreases even more strongly in the production of alcohols from hydrocarbons (reaction 1) and α -oxides from olefins (reaction 9), but it is still rather high.

The data given above allow one to compare the exothermicity of oxidation processes effected by means of various oxidizing agents. For example, the oxidation of toluene by nitric acid (reaction 12) is accompanied by the evolution of a lower amount of heat than its oxidation by molecular oxygen (reaction 4). This difference is due to the fact that oxides of nitrogen belong to the class of endothermic compounds and their formation reduces the overall heat effect. Epoxidation processes carried out with hydrogen peroxide or peracetic acid (reactions 10 and 11) are, on the contrary, more exothermic than with molecular oxygen (reaction 9). This is accounted for by the exothermicity of the decomposition of H_2O_2 and CH_3COOOH which yields oxygen and water and acetic acid, respectively.

It should be noted that the overall heat effect of many industrial oxidation processes, which are often accompanied by complete oxidation, has been found to be much higher than that given above. It can be calculated if the fraction of various reactions or the composition of the products is known.

6.2. Homogeneous Oxidation at the Saturated Carbon Atom

The oxidation at the saturated carbon atom is classified into three groups of processes:

- (1) oxidation of paraffinic hydrocarbons and their derivatives;

- (2) oxidation of cycloparaffins and their derivatives;
- (3) oxidation of the side chains of alkylaromatic hydrocarbons.

The end products of these processes in various cases are hydroperoxides, alcohols, aldehydes, ketones, carboxylic acids and their anhydrides.

6.2.1. Scientific and Engineering Foundations of Oxidation Processes

The oxidation at the saturated carbon atom is mostly effected using molecular oxygen in the liquid phase and less frequently in the vapour phase under the conditions of a homogeneous process. These reactions are radical-chain processes and they may be divided into two groups: thermal reactions (autoxidation) and reactions catalyzed by salts of metals of variable valency (Co, Mn, etc.).

6.2.1.1. The Mechanism of Formation of Oxidation Products

The oxidation of hydrocarbons gives a large variety of molecular products: hydroperoxides, alcohols, ketones, aldehydes, carboxylic acids, esters and some more complex polyfunctional compounds. The intermediate active particles are radicals with free valency on the carbon atom $R\cdot$ or on oxygen atoms ($ROO\cdot$, $RCOOO\cdot$).

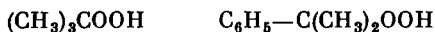
Hydroperoxides. These are the initial molecular products of the oxidation of hydrocarbons. The chain step during their formation is¹ as follows:



The last reaction—the interaction of the peroxide radical with the hydrocarbon—determines the structure of the hydroperoxide being formed and of the subsequent oxidation products. The order of variation of the reactivity of hydrogen atoms, which is determined by the relative stability of the intermediate radical $R\cdot$, is analogous to the order typical of radical reactions. As a consequence, the molecule preferentially attacks the α -position of the side chain relative to the aromatic ring during the oxidation of arylalkanes; in the case of olefins the preferential site of attack is the allylic position. Moreover, for hydrocarbons of all classes there holds the known order of variation of the replaceability of hydrogen atoms on various carbon atoms (tertiary > secondary > primary).

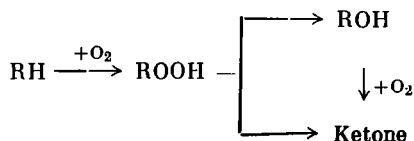
Hydroperoxides belong to the class of rather unstable compounds which are converted on oxidation into other products. Therefore, their concentration in the reaction mass, especially on catalytic oxidation or at elevated temperatures, is not high. Primary hydroperoxides (RCH_2OOH or $ArCH_2OOH$) are the most unstable and, on the contrary, tertiary hydroperoxides are relatively stable; of

tertiary hydroperoxides, the hydroperoxides of *tert*-butyl and isopropylbenzene



are industrial products. Of secondary compounds, the hydroperoxides of cycloalkanes in the range $\text{C}_8\text{--C}_{12}$, olefins and arylalkanes are relatively stable.

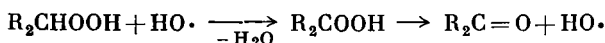
Alcohols and Carbonyl Compounds. These compounds are the next products of the oxidation of hydrocarbons. Alcohols are produced in a considerable quantity only by the oxidation of paraffins and naphthenes, but not from alkylaromatic compounds. According to the traditional Langebek-Pritzkow scheme, these products are formed on oxidation via a hydroperoxide:



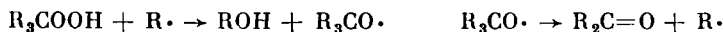
When hydroperoxides decompose under the action of elevated temperature or of oxidation catalysts, they do form alcohols and carbonyl compounds. This decomposition may proceed by a molecular mechanism, but in the developed oxidation process the products are formed predominantly by the chain route. In the production of alcohols the chain step is as follows:



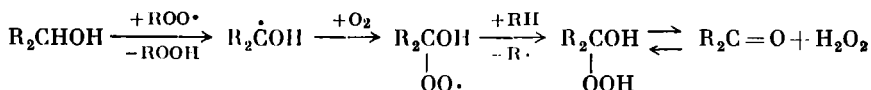
Ketones are formed from secondary hydroperoxides via the step of radical-hydroperoxides:



Tertiary hydroperoxides on chain conversion give not only an alcohol with the same number of carbon atoms but also an alcohol and a ketone with a lesser number of carbon atoms due to the disruption of the carbon-carbon bond:

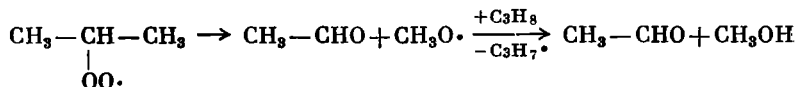
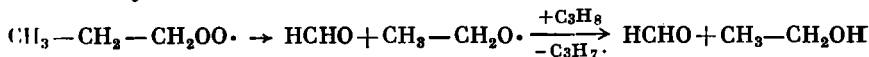


Alcohols are also converted to ketones by a chain route; here the carbon atom that has already been affected by the oxidation is attacked in the alcohol molecule:

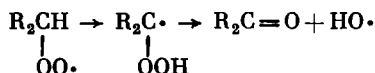


The reaction mechanisms considered above are mainly characteristic of the noncatalytic oxidation in the liquid phase at moderate

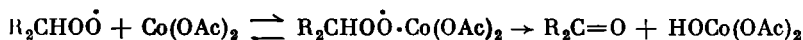
temperatures. In a high-temperature oxidation in the vapour phase all the products are formed via peroxide radicals, without the formation of hydroperoxides, the process involving a considerable disruption across the carbon-carbon bond, with the formation of alcohols and aldehydes:



It has lately been found that peroxide radicals play an important role in the formation of products in liquid-phase oxidations. For instance, carbonyl compounds can be prepared from peroxide radicals in the following way:

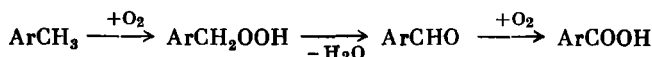


On catalysis with salts of metals of variable valency the metal ions can react with peroxide radicals to give complexes, which are converted in the coordination sphere of the central ion, this ion being oxidized to a higher valent state:

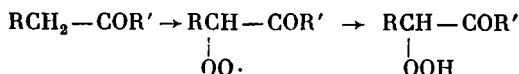


Thus, alcohols and carbonyl compounds can be obtained in the liquid-phase oxidation not only consecutively but also concurrently with the formation of a hydroperoxide.

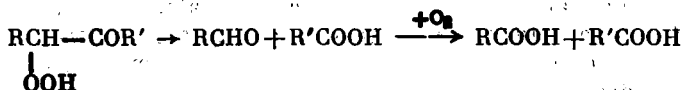
Carboxylic Acids. These acids are formed on oxidation of hydrocarbons with retention of their carbon chain or with disruption of the carbon-carbon bond. The former is possible only on conversion of primary hydroperoxides and is typical only of the oxidation of the methyl groups of alkylaromatic compounds via the intermediate aldehyde step:



The oxidation of paraffins and naphthenes involves the disruption of the carbon chain and gives carboxylic acids. It is most probable that the precursors of the acids are ketones. They are oxidized more readily than the corresponding hydrocarbons and preferentially at the carbon atom adjacent to the carbonyl group, forming an α -ketoperoxide radical and an α -ketohydroperoxide:

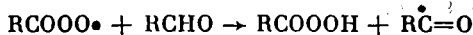
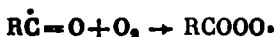


Evidently, the C—C bond is broken at this stage; for example,

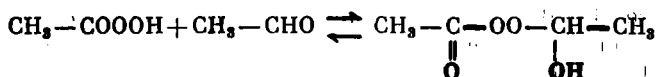


The lower aliphatic and aromatic acids are stable towards further oxidation at moderate temperatures.

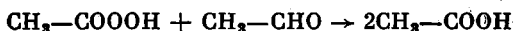
Aldehydes. Aldehydes are the most readily oxidizable compounds; when hydrocarbons are oxidized in the liquid phase, aldehydes are either formed in a small amount or cannot be detected at all in the reaction products. In a radical-chain oxidation aldehydes give intermediate acyl and peracyl radicals and a peracid:



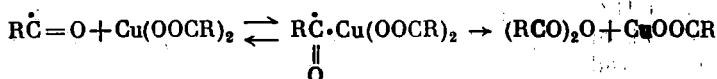
The peracid is capable of adding on to aldehydes with the formation of a peroxide compound, which is called acetaldehyde peracetate in the case of the oxidation of acetaldehyde:



The equilibrium of this reaction is significantly shifted to the right at a low temperature and under these conditions without catalysts or in the presence of a small amount of the catalyst the peracetate becomes the end oxidation product. On heating and in the presence of salts of metals of variable valency the peracetate decomposes rapidly and gives two molecules of the carboxylic acid. Under the conditions indicated the amount of peracetate formed is insignificant and the reaction boils down to the oxidation of the aldehyde by peracetic acid:

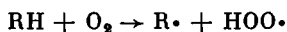


Apart from the peracid and carboxylic acid, anhydrides are also the oxidation products of aldehydes. Their formation is favoured by the use of a mixed catalyst (salts of Co or Mn with salts of Cu) and by a reduced partial oxygen pressure. One of the possible mechanisms of the formation of anhydrides involves the conversions of the acyl radical in the coordination sphere of the copper atom:



The resultant cuprous salt is again oxidized by the peracid to the higher valent state.

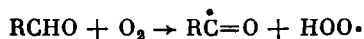
Kinetics and Catalysis of Homogeneous Oxidation. The homogeneous radical-chain oxidation consists of the initiation, propagation, termination and branching of the chain. The primary formation of radicals on oxidation occurs upon addition of initiators to the mixture (the initiators used are hydroperoxides and peroxides, and azobisisobutyronitrile in the liquid phase and HNO_3 , NO and HBr in the vapour phase) upon autoxidation of an organic compound:



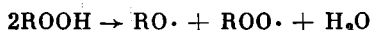
or upon interaction of oxygen with the catalyst:



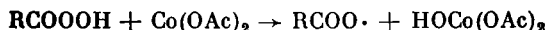
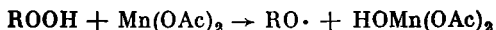
In a developed oxidation process other sources of radicals come into scene, among which a significant role is assigned to degenerate branching of the chain. In a high-temperature oxidation in the gas phase degenerate branching occurs as a result of the oxidation of reactive aldehydes:



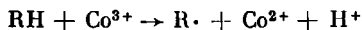
and at moderate temperatures of liquid-phase processes it occurs by way of the decomposition of hydroperoxides or peracids:



The last reaction is accelerated by salts of metals of variable valency (acetates or naphthenates of cobalt, manganese, etc.), this being the traditional explanation of their catalytic action upon homogeneous oxidation in the liquid phase:

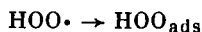


Moreover, the formation of radicals may occur as a result of the oxidation of hydroperoxides, aldehydes or even of hydrocarbons by the highest valent form of the catalyst:



The chain propagation step upon formation of various oxidation products has been considered above.

The chain termination in gas-phase oxidation reactions usually occurs linearly upon collision of the peroxide radical with the wall:

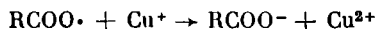


The liquid-phase oxidation involves a quadratic chain termination on the least reactive peroxide or peracyl radicals:



Just as in other radical-chain processes, chain termination may occur on inhibitors (sulphur compounds, phenols). In the presence of such impurities in the raw material there is observed a more or less prolonged induction period of oxidation, which becomes shorter upon addition of initiators or catalysts, but in order to avoid the retardation of the process, the feedstock to be oxidized must be of high purity.

The salts of metals in the lowest valent state may also serve as inhibitors, which is accounted for by their reaction with peroxide radicals; an example is



As a result, the induction period, which usually becomes shorter upon addition of such salts, may increase with increasing concentra-

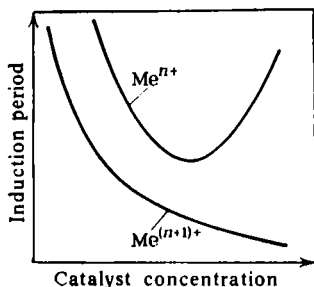


Fig. 6.1. The effect of the catalyst concentration on the duration of the induction period of oxidation.

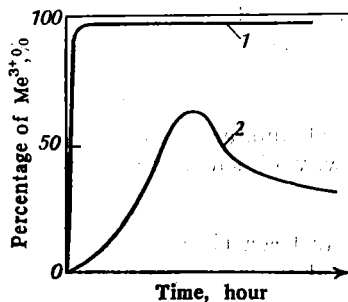
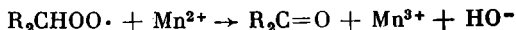


Fig. 6.2. The change of the state of the catalyst during the liquid-phase oxidation of isopropylbenzene and tetralin (1) and paraffins and naphthenes (2).

tion of the salt (Fig. 6.1), whereas with salts of metals in their highest valence state the duration of the induction period decreases steadily with increasing concentration of the salt. Still, the catalytic role of metals of variable valency prevails over their inhibiting function, which is why the use of these catalysts in the liquid-phase oxidation processes is successful.

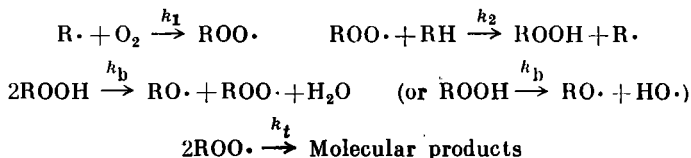
An ever increasing role in the formation of liquid-phase oxidation products is assigned to reactions of radicals with ions of metallic catalysts. These are chain termination reaction, but with a sufficiently rapid catalyst regeneration step they become an important route to products:



Here the ion of the metal-catalyst begins to participate in the chain propagation step, and its role in branching becomes less significant.

In a developed oxidation process the rates of the above-given steps of formation and consumption of various valent forms of the catalyst are equal, which leads to steady-state concentrations of these forms during the course of the reaction. Here the initially introduced cobaltous (or manganous) salt sometimes remains unchanged, but in most cases it is partially or completely oxidized (Fig. 6.2), the oxidation being accompanied by a change in the colour of the solution.

In practice, the noncatalytic oxidation in the liquid phase is employed only for the synthesis of hydroperoxides and peracids (since peracids are capable of decomposition under the influence of catalysts). In this case, the kinetics of the process is determined by the following elementary steps:



Using the steady-state method, we obtain:

$$r = k_2[\text{ROO} \cdot][\text{RH}] = k_2 \sqrt{\frac{k_b}{k_t}} [\text{RH}][\text{ROOH}]^{n/2}$$

where n is the order of the reaction of decomposition of the hydroperoxide. Hence, the rate of oxidation is usually independent of the concentration and partial pressure of oxygen, but when these decrease strongly the rate of the first chain propagation step may fall off to such an extent that the second reaction will be rate-limiting and chain termination will occur at the alkyl radicals:

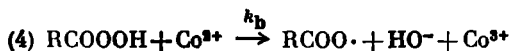
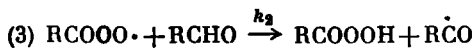
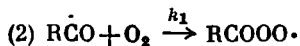
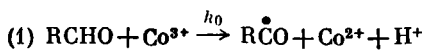


As a result, in an analogous way we obtain the following equation:

$$r = k_1 \sqrt{\frac{k_b}{k_t}} [\text{O}_2][\text{ROOH}]^{n/2}$$

Thus, under different conditions of chain termination the dependence of the reaction rate on the partial oxygen pressure is depicted by a curve with saturation (Fig. 6.3), which usually occurs at a pressure of ≈ 100 GPa. From the relationships obtained it can be seen that upon thermal oxidation in the liquid phase, the initial oxidation step can be favourably intensified by addition of a ready hydroperoxide to the initial mixture, which is often done in practice.

For example, for the catalytic oxidation of aldehydes the kinetics of the process is determined by the following elementary steps:



The steady-state concentrations of various oxidation states of the catalyst require the equality of the rates of steps 1 and 4. Since the

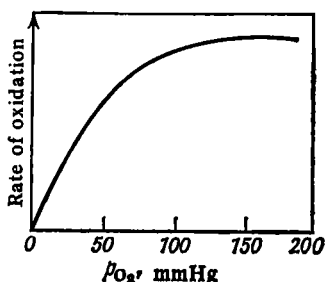


Fig. 6.3. Dependence of the rate of the homogeneous oxidation on the partial pressure of oxygen: 1 mm Hg = 133.322 Pa.

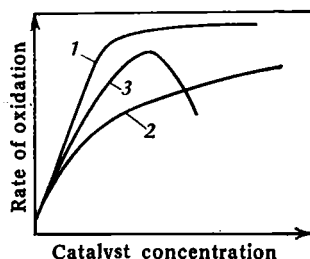


Fig. 6.4. The effect of the catalyst concentration on the rate of the liquid-phase oxidation of paraffins in the presence of Co^{2+} (curve 1) and Mn^{2+} (curve 2) and on the rate of the oxidation of alkylaromatic hydrocarbons in the presence of Co^{2+} (curve 3).

slowest step is the first step and the entire catalyst is practically in the trivalent state, the overall rate of the process will be equal to

$$r = k_2[\text{RCOOO}^\bullet][\text{RCHO}] = k_2 \sqrt{\frac{k_0}{k_t}} [\text{Co}^{3+}]^{0.5} [\text{RCHO}]^{1.5}$$

The fractional dependence of the rate on the catalyst concentration is typical of many liquid-phase oxidation processes, including the oxidation of hydrocarbons. Sometimes there is observed a slowly retarding increase of the reaction rate or even its decrease at high catalyst concentrations. At the same time cases are known where the velocity is linearly dependent on the catalyst concentration (Fig. 6.4) or even has a quadratic dependence.

The activation energy in the homogeneous-catalytic oxidation of hydrocarbons in the liquid phase is 50-84 kJ/mol (12-20 kcal/mol);

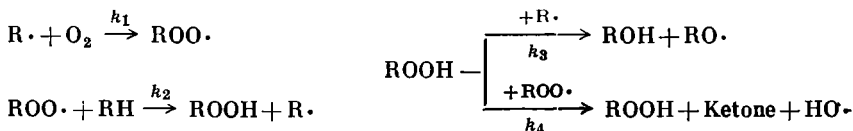
for thermal or initiated oxidations it is equal to 105-147 kJ/mol (25-35 kcal/mol). Here the reactivity of hydrocarbons of various classes varies in the sequence usual for radical-chain reactions:



Selectivity of Homogeneous Oxidation. The selectivity of homogeneous oxidation reactions depends on the development of parallel and consecutive conversions during the formation of end products and by-products. Parallel conversions may in turn be dependent on two factors: reactions at various carbon atoms in the molecule of the reactant or the parallel formation of compounds having different functional groups.

The former reactions depend on the relative reactivity of various hydrogen atoms when they are attacked by the peroxide or other oxygen-containing radical. In this respect the radical-chain oxidation is noted for a relatively high selectivity, which is determined by the low activity of peroxide radicals. For example, the reactivities of hydrogen atoms in the tertiary, secondary and primary positions in the molecule stand in the ratio 100 : 10 : 1. This allows one to obtain, for example, *tert*-amylhydroperoxide with a satisfactory selectivity in the presence of three types of hydrogen atoms in isopentane and the products of the conversion in secondary positions upon oxidation of *n*-paraffins.

The parallel formation of compounds with different functional groups (for example, the formation of alcohols and ketones from hydrocarbons and of carboxylic acids and anhydrides from aldehydes) can be controlled not infrequently by choosing the appropriate process parameters. For instance, the relative yield of alcohols and ketones is determined by the following elementary steps:



which are responsible for the following relationship between the concentrations of radicals and the yields of alcohol and ketone:

$$\frac{[\text{R}\cdot]}{[\text{ROO}\cdot]} = \frac{k_2[\text{RH}]}{k_1[\text{O}_2]} \quad \frac{d[\text{ROH}]}{d[\text{Ketone}]} = \frac{k_3[\text{R}\cdot]_i^2}{k_4[\text{ROO}\cdot]} = \frac{k_2k_3[\text{RH}]}{k_1k_4[\text{O}_2]}$$

Thus, the relative yield of the alcohol can be increased with decrease of the partial oxygen pressure in the oxidizing gas. The same phenomenon in the oxidation of aldehydes leads to an increase in the yield of the anhydride at the expense of the carboxylic acid.

Consecutive conversions play an important role in radical-chain oxidation processes. Apart from the products indicated above, the

radical-chain oxidation may give hydroxyketones, diketones, hydroxy- and ketocarboxylic acids, esters, lactones, etc. Finally, the complete oxidation to CO_2 is also observed. The principal means of reducing the extent of these side reactions is control of the degree of conversion. In this respect all radical-chain oxidation processes are divided into two groups:

1. Processes in which the desirable end products are stable towards further oxidation (lower aliphatic and aromatic acids); the degree of conversion plays no important role with respect to selectivity, though it may have an effect on the other parameters (it may slow down the reaction and favour the deposition of the catalyst). The degree of conversion may vary (amounting to 95-99 percent), and the intermediate can be recycled to oxidation together with the unconverted reagent.

2. Processes leading to the directed synthesis of intermediates which are liable to decompose or to be oxidized (the production of hydroperoxides, alcohols, ketones, higher carboxylic acids); the degree of conversion plays a very important role and it is limited in various cases to the range of 5-30 percent. The cost of the recovery and recycling of the unchanged reagent is substantial and these processes must be optimized with account taken of changes in selectivity with various degrees of conversion.

The selectivity is strongly affected by temperature, this being dependent on the activation energies of the various steps of the process (the activation energy is usually higher for side reactions). As a result, each process has a certain optimum temperature determined by the attainment of the adequate oxidation rate and selectivity. An increase in temperature may play another negative role, i.e., be responsible for the process being switched over into the diffusional or near-diffusional region: the process takes place in the boundary film and the intermediates have no chance to diffuse into the bulk of the liquid and become overoxidized. Therefore, an important role is played by the effective agitation of the reaction mixture upon bubbling of the oxidizing gas: such agitation contributes to the switchover of the process into the kinetic region, the attainment of a large interfacial contact and to the intensification of the process. Hence, the choice of oxidation conditions is a complicated function of many chemical and technological factors.

6.2.1.2. Reactors for Liquid-Phase Oxidation Processes

The overwhelming majority of oxidation processes are effected in the liquid phase by bubbling the air (less frequently, technical oxygen) through the organic reagent, in which the reaction products are gradually accumulated. While the choice of temperature depends on the intensity and selectivity of the process, the pressure is chosen

mainly with a view to maintaining the reaction mass in the liquid state.

The industrial reactors most frequently used are bubble columns up to 10-15 m high and up to 2-3 m in diameter; in some cases the reactors are divided into sections by horizontal sieve or cap plates or connected into cascades. Since carboxylic acids cause the corrosion of ordinary steel, the reactors are constructed of aluminium, titanium or special grades of steel resistant to the action of organic acids.

The manner in which the large amount of heat evolved is removed is an important factor. There are systems with internal heat exchangers, which complicates the design of the reactor. Reactors with external heat exchangers and circulation of the liquid through them are more preferable. It is more favourable to remove the heat by the evaporation of the hydrocarbon feed or solvent, which are condensed in a reflux condenser and are returned to the reactor. Finally, in newer units operating at temperatures higher than 150 °C steam is generated due to the reaction heat and the pressure is used for a partial separation of the mixture, for producing the cold, etc.

Figure 6.5a shows a typical oxidation batch reactor with external cooling due to the circulation of the liquid through a water cooler. The circulation may also be effected in the opposite direction; it may occur naturally due to the difference in the density of the liquid in the column and in the circulation circuit. The reagent is charged into the reactor upon completion of the preceding operation and heated to the required temperature (at this time steam is introduced into the cooler instead of water) and the air is admitted into the reactor. The air distribution is effected by a perforated pipe or a sieve or grid tray.

The continuous process in a single bubble column can be carried out when the end products are stable towards further oxidation (acetic acid, aromatic acids). In this case, the compound to be oxidized and the air are introduced into the bottom of the reactor (concurrently) and the products are withdrawn at the side (Fig. 6.5b). The heat is removed by any of the methods indicated above, but Fig. 6.5b shows only internal coolers.

If the selectivity of the process depends strongly on the degree of conversion of the reagent, a single bubble column becomes unfavourable for the continuous process because of the vigorous stirring of the liquid. Figure 6.5c shows a cascade of bubble columns: the liquid reaction mass overflows from one column to another and the air is admitted separately into each of them. The heat is removed here by the evaporation of the hydrocarbon or solvent. Their vapours are condensed in reflux condensers which are located above each of the columns, and the condensate runs down into the reactor.

Figure 6.5*d* shows another type of a continuous oxidation reactor, a tray column. In this column, the liquid flows downwards from one tray to another and the air moves countercurrently upwards. Cooling is effected by passing water into the coils placed in a layer of the liquid at each tray. External cooling is also possible, in which case the liquid from each tray circulates through a separate cooler.

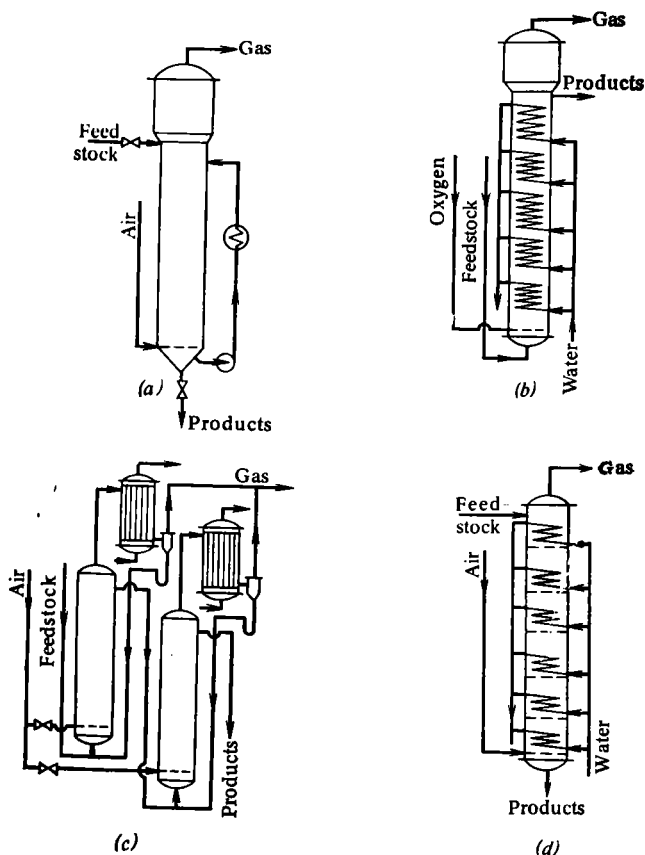


Fig. 6.5. Reaction units for the liquid-phase oxidation by molecular oxygen: *a*—batch reactor with an external cooler; *b*—continuous reactor with an internal cooler; *c*—cascade of columns with cooling by evaporation; *d*—tray column.

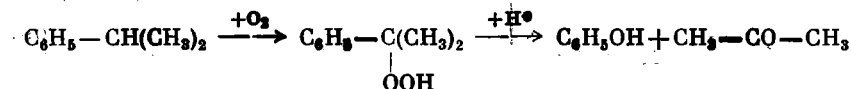
In all batch and continuous reactors the oxidation conditions are controlled by changing the rate of feed of the oxidizing gas and the organic reagent. The temperature is usually measured at several points along the height of the reactor; the reaction mass is periodically analyzed.

In liquid-phase oxidation processes, it is necessary to prevent the formation of explosive mixtures at points where there is a continuous gas phase (i.e., in the upper part of the bubble columns and in the space above each tray in a reactor of the type shown in Fig. 6.5*d*). This is achieved by a high degree of conversion in conjunction with the choice of the pressure, depending on the volatility of the organic feed. Sometimes nitrogen is admitted into the space above the liquid. The fire and explosion hazards in the manufacturing processes considered (except for the oxidation of hard paraffin wax) are nevertheless rather significant and these industries must be equipped with the most modern means for the prevention, localization and extinguishing of fires.

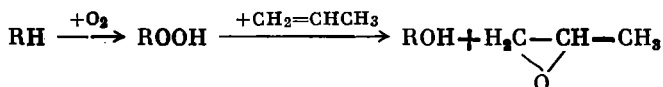
6.2.2. Oxidation of Hydrocarbons to Hydroperoxides.

Production of Phenol and Acetone

The first large-scale production of hydroperoxides was started in the USSR in 1949 as a part of the cumene method of manufacture of phenol and acetone discovered by P. G. Sergeev, B. D. Kruzhalov and R. Yu. Udris:



Some hydroperoxides are used as polymerization initiators; their significance has lately increased in connection with the development of a new process of epoxidation of olefins:



6.2.2.1. Production of Hydroperoxides

Isopropylbenzene hydroperoxide (cumene hydroperoxide) is produced industrially on the largest scale; the hydroperoxides of *m*- and *p*-cymene (isopropyltoluene) and of *m*- and *p*-diisopropylbenzene are produced on a lesser scale and are further converted into phenol, *m*- and *p*-cresols, resorcinol and hydroquinone, respectively. The epoxidation of olefins is effected by using mainly ethylbenzene and *tert*-butyl hydroperoxides, and for one of the methods of isoprene synthesis *tert*-amylhydroperoxide is required as the feedstock. All these compounds are relatively stable, especially in solutions of starting hydrocarbons; in this form they are used not infrequently in further processing. But hydroperoxides are also made in concentrated form (80-95 percent); in such cases, special safety measures are necessary for handling them (the absence of overheating and decomposition catalysts—metals of variable valency and their salts, acids).

The oxidation of hydrocarbons gives hydroperoxides by the above-considered radical-chain mechanism. Inhibitors (phenol, olefins, sulphur compounds) strongly retard the process, leading to the appearance of an induction period, which is why the starting hydrocarbons must be thoroughly purified from undesirable impurities. For example, isopropylbenzene obtained

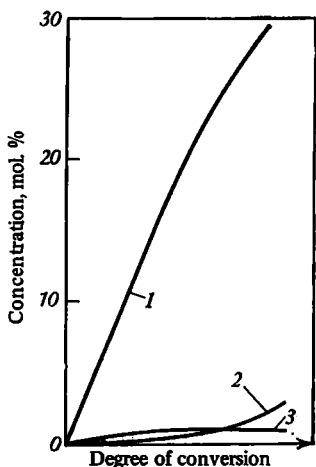


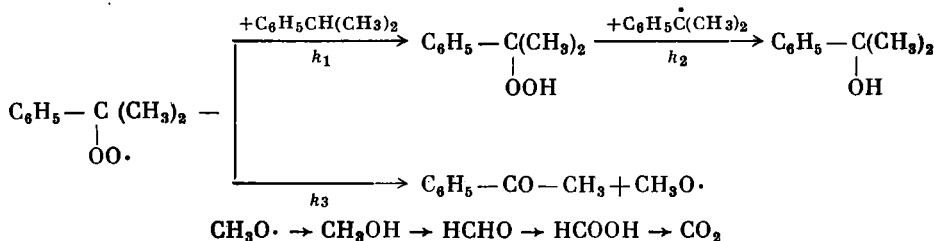
Fig. 6.6. The curves of accumulation of the oxidation products of isopropylbenzene:

1—*isopropylbenzene hydroperoxide*; 2—*dimethyl phenyl carbinol*; 3—*acetophenone*.

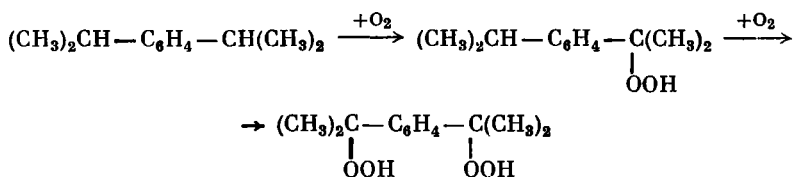
by alkylation in the presence of a solid phosphoric-acid catalyst is not suitable for oxidation. The elimination of the induction period and the acceleration of the reaction at its initial stages are favoured by addition of the hydroperoxide or the reaction mass containing the hydroperoxide to the feedstock. The salts of metals of variable valency, which are ordinary catalysts of homogeneous oxidation, decompose hydroperoxides and are not therefore used for this reason, though in some isolated cases the addition of small amounts of such salts speeds up the reaction. The same effect is provided by metallic copper if it is used in the form of filings or even if it

is present in the material of the equipment. It has been reported that the reaction can be catalyzed by salts of metals of constant valency (sodium, potassium and magnesium).

The production of hydroperoxides always involves the formation of by-products, chiefly alcohols and, to a lesser extent, ketones. For instance, the oxidation of cumene gives phenyl dimethyl carbinol and acetophenone; the character of the kinetic curves (Fig. 6.6) shows that the alcohol is formed consecutively in the conversion of the hydroperoxide and the ketone is formed concurrently from the peroxy radical:



Analogously, the oxidation of ethylbenzene gives phenyl methyl carbinol, $C_6H_5-CH(OH)CH_3$, and acetophenone; from isobutane *tert*-butyl alcohol, acetone and methanol are obtained. The oxidation of *m*- and *p*-isopropyltoluene gives not only the end hydroperoxide of tertiary structure and the corresponding by-products but also the primary hydroperoxide $(CH_3)_2CH-C_6H_4-CH_2OOH$ and its decomposition products, which lowers the selectivity of the reaction. When *m*- or *p*-diisopropylbenzene is oxidized, mono- and dihydroperoxides are successively produced:



This process yields a large number of by-products: an alcohol and a diol, a ketone and a diketone, and hydroxy- and ketohydroperoxides.

The selectivity with respect to the hydroperoxide is increased mainly by a decrease in temperature and degree of conversion; these parameters are kept at an optimum level, which depends on the overall economic efficiency of the process. For example, the temperature in the oxidation of alkylaromatic hydrocarbons is maintained within the range 100-120 °C and the oxidation of isobutane is carried out at 120-150 °C. It is useful to lower the temperature as the hydroperoxide is formed in order to slow down its decomposition. The successive conversions of the hydroperoxide can be prevented by limiting the degree of conversion to the range from 30 percent (in the oxidation of cumene) up to 10 percent (for ethylbenzene); in the production of diisopropylbenzene dihydroperoxide the degree of conversion has to be increased up to 50-60 percent.

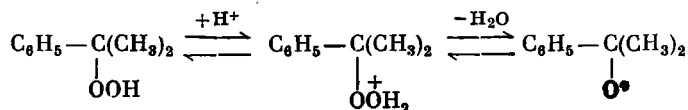
Alkylaromatic hydroperoxides are mainly produced by using reactors of the tray-column type (see Fig. 6.5d) with the counter-current flow of the liquid and the gas, the heat being removed by means of internal coils placed on the column trays. The oxidation is carried out with air at a pressure from 0.3 to 0.5 MPa for isopropylbenzene up to 5-8 MPa for isobutane (in the latter case, the pressure is required in order to maintain the mixture in the liquid state and to reduce the loss of the compound with the effluent gas). Another method of oxidation, which is widely employed in the USA, is to carry out the process in a water-hydrocarbon mixture with addition of Na_2CO_3 ; the oxidation is effected in a cascade of bubble-cap reactors, the heat being removed by the evaporation of water. Addition of small amounts of Na_2CO_3 (or NaOH) is also useful when the oxidation is accomplished by the first method. The function of alk-

lis is to neutralize formic acid formed as a by-product; the neutralization prevents the acidic decomposition of the hydroperoxide (with the formation of phenols) and the dehydration of carbinols (with the formation of homologues of styrene). Like phenols, the homologues of styrene are oxidation inhibitors.

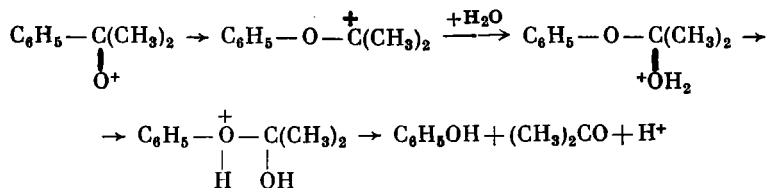
The resultant solution of the hydroperoxide and by-products in the hydrocarbon feedstock is usually "strengthened" or concentrated by distillation of the hydrocarbon. For this purpose, a sufficiently deep vacuum is used in the production of alkylaromatic hydroperoxides. In order to reduce the residence time of the hydroperoxide at elevated temperatures and to lower the degree of its decomposition, it is suggested that the hydrocarbon be distilled off in film apparatus.

6.2.2.2. Acidic Decomposition of Hydroperoxides

Apart from the free-radical route of decomposition, alkylaromatic hydroperoxides are also capable of undergoing decomposition under the influence of acidic and alkaline catalysts. In the presence of even a small amount of a strong acid (say, 0.1 percent of H_2SO_4) hydroperoxides decompose with the formation of phenols and carbonyl compounds. The reaction proceeds by a complicated ionic mechanism with the intermediate formation of positively charged ions:



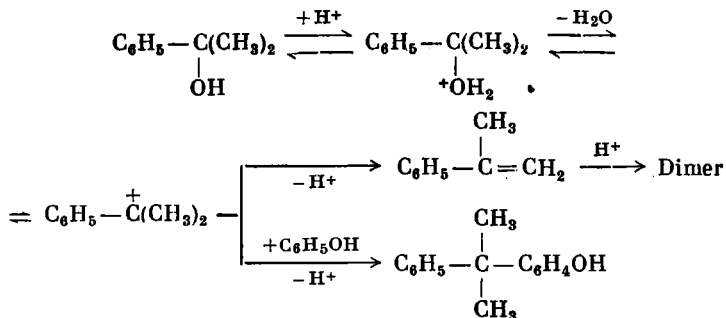
The resulting ion rearranges with the phenyl group migrating to the oxygen atom, this being followed by conversions, as a result of which phenol and acetone are produced:



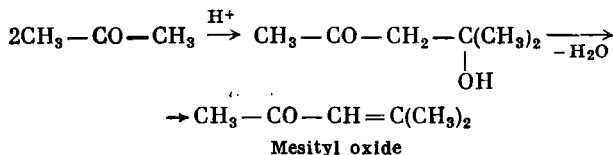
With a different structure of the *sec*-alkyl group there are formed the homologues of acetone (methyl ethyl ketone) and the hydroperoxides of *n*-alkylbenzenes—acetaldehyde and its homologues.

The oxidation by-products contained as impurities in the hydroperoxide (especially phenyl alkyl carbinols) are also sensitive to acidic catalysis. For instance, when cumene hydroperoxide breaks up, phenyl dimethyl carbinol splits off water, forming α -methylstyrene, and alkylates phenol with the formation of cumylphenol.

Besides, α -methylstyrene undergoes partial dimerization:



There is also obtained a small amount of resins of a more complex structure. An increase in acid concentration and temperature makes it possible to effect acid-catalytic conversions of acetophenone and acetone, say by a reaction of the aldol condensation type with subsequent splitting-off of water:



In kinetic respect the acidic decomposition of the hydroperoxide is characterized by a very high velocity, the practically complete conversion in the presence of 0.05-1 percent (by weight) of H_2SO_4 (based on hydroperoxide) at 50-60 °C being achieved in 2-3 min. The reaction is slowed down by water and accelerated by the phenol formed and is first-order in both the acid catalyst and the hydroperoxide. Cation-exchange resins have also been tested as catalysts, but no information is available on their practical application.

When the process is carried out industrially, the removal of a large amount of heat evolved is very important because of the high velocity of the reaction: the heat evolved is 2080 kJ (486 kcal) per 1 kg of hydroperoxide. For this purpose, use is primarily made of diluents, the role of which is played by the reaction products or acetone.

One of the methods of carrying out the reaction consists of the use of a flow-circulation unit (Fig. 6.7a); the heat evolved is removed in a tubular reactor due to cooling with water. The reaction mixture leaving the reactor is partly sent for further processing, but the major proportion is led to recirculation: the acid catalyst is added and the reaction mass is mixed with the hydroperoxide feed in a pump. With such a system the contact time is limited by the heat removal and is too long. Moreover, the recycling of the mixture results in

an increased yield of by-products. For example, for 1 ton of phenol there is obtained 100-150 kg of wastes, including 15-20 kg of α -methylstyrene, 40-50 kg of dimer and resins, 5-10 kg of acetophenone, 30 kg of cumylphenol, etc. Though mesityl oxide is formed in a small amount, it still complicates substantially the purification of phenol.

A further method of acidic decomposition of hydroperoxides (Fig. 6.7b) is to effect the reaction in a solution of acetone and to remove the heat by way of its evaporation. Acetone is condensed

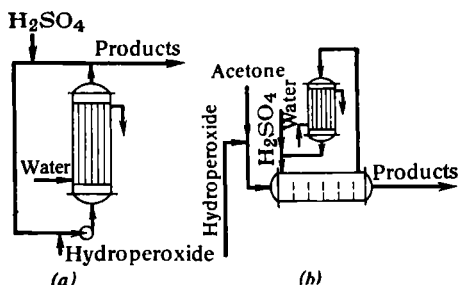


Fig. 6.7. Reaction units for the acidic decomposition of hydroperoxides: a—flow-circulation unit; b—unit with heat removal by evaporation of acetone.

in a reflux cooler and returned to the reactor, which can be divided into sections by lateral partitions. Apart from reducing the concentration of phenol in solution and the time of contact, this also lowers the yield of by-products.

6.2.2.3. Products Obtained by Acidic Decomposition of Hydroperoxides

Phenol, carboic acid, C_6H_5OH , is a crystalline substance (m.p. 42 °C, b.p. 181.4 °C). When freshly prepared it is colourless, but on storage it turns pink or red. Phenol is highly toxic and, besides, irritates the skin.

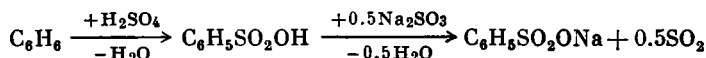
The applications of phenol as an intermediate of organic synthesis are diverse. It is used in the production of dyes, pharmaceuticals and explosives. The synthesis of chlorophenols and also of herbicides and bactericide preparations based on chlorophenols has already been described. Phenol is alkylated to produce antioxidation additives and intermediates for the synthesis of nonionic surfactants. Especially large quantities of phenol are consumed for the manufacture of phenol-aldehyde polymers, the synthetic fibres capron and nylon (amide), epoxy polymers and polycarbonates.

The original route to phenol was its derivation from coal tar formed during the coking of coal. But, because of the low yield of phenol (≈ 0.05 kg per 1 ton of coal), it was impossible to satisfy

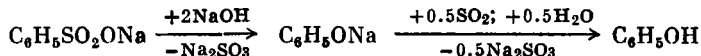
the increasing demands for this product. At present, the proportion of coal-derived phenol is not high in the overall balance and continues to fall off. Of prime importance are the synthetic methods of phenol production, which may be classified into three groups: the chlorine, sulphonation and oxidation methods.

The chlorine methods have already been considered (page 189); they consist of the alkaline hydrolysis of chlorobenzene or of its steam hydrolysis combined with the oxidative chlorination of benzene (the Raschig process).

The sulphonation process was the first of the synthetic processes for the manufacture of phenol and is still operated today. It consists of the sulphonation of benzene followed by caustic fusion of the sulphonate at 300-350 °C. The sulpho mass is neutralized by sodium sulphite obtained at the caustic fusion step:



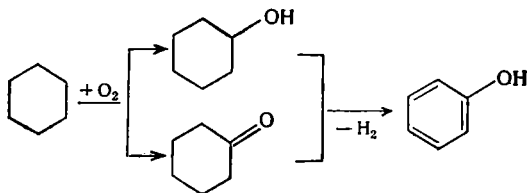
The sulphonate is then mixed with a concentrated solution of caustic and caustic fusion is carried out; this gives sodium phenate and sulphite. Free phenol is isolated from the phenate by sulphur dioxide formed at the step of neutralization of the sulpho mass, for which purpose part of the Na_2SO_3 is used:



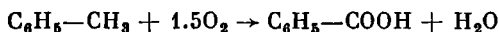
Owing to the use of the co-products formed at some steps of the process, the quantities of the feedstock consumed and wastes formed in other operations are considerably reduced, but they still remain to be large.

The sulphonation process has been replaced in the last two decades by the cumene method. The advantages of the cumene process are the consumption of a small amount of a cheap raw material (apart from benzene, practically only air is used) and the combined production of two valuable products—phenol and acetone.

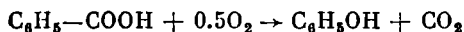
There are other oxidation processes used commercially for the manufacture of phenol. One of them is based on the processing of cyclohexane, which is oxidized to a mixture of cyclohexanol and cyclohexanone. These compounds are dehydrogenated to phenol over platinized carbon at 250-425 °C in high yield:



In a further method that has lately been developed and realized industrially (the toluene process), the feedstock is toluene, which is more available than benzene and has not so many outlets as benzene. Toluene is first oxidized to benzoic acid in the liquid phase in the presence of salt catalysts:



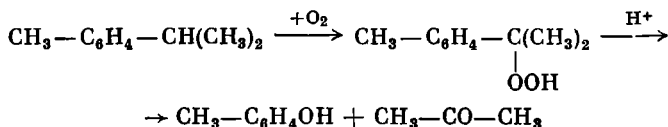
The benzoic acid is then converted to phenol by way of the liquid-phase oxidation with air (mixed with steam) at 230 °C using a homogeneous catalyst of cupric benzoate promoted with magnesium benzoate:



The various methods of phenol synthesis are compared below (in arbitrary units per 1 ton of phenol):

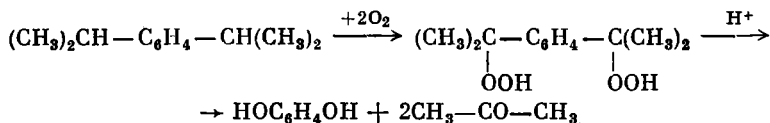
Process	Capital investment	Cost of feedstock (minus the products utilized)	Cost of phenol
Chlorobenzene	9.4	162.2	188.4
Raschig	27.1	89.5	137
Sulphonation	11.3	154.5	196.1
Cumene	22.8	69.6	109.7
Oxidation of toluene	22.8	106.6	142.8
From benzene via cyclohexane	23.5	110.6	148.3

The oxidation process is also used to produce *m*- and *p*-cresols via *m*- and *p*-cymene hydroperoxides:



The uses of cresols and other methods of their production have been described earlier (page 274). The methods of their manufacture by way of the methylation of phenol and via the hydroperoxide are presumably comparable from the economic standpoint.

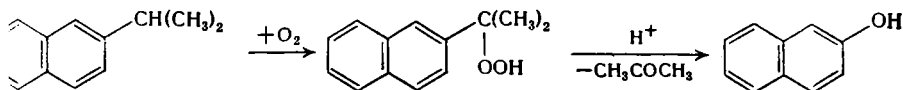
Hydroquinone and *resorcinol* are made from the dihydroperoxides of *m*- and *p*-diisopropylbenzene:



Resorcinol (*m*-dihydroxybenzene) was made in the past via *m*-benzenedisulphonic acid. Because of the increasing application of resorcinol (for the production of readily solidifiable phenol-aldehyde

polymers) and of hydroquinone (as an inhibitor), the oxidation process for their production becomes increasingly important in the industry.

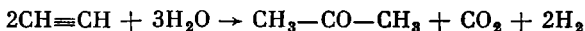
β -Naphthol, which is important in the production of dyes, is produced via β -isopropyl-naphthalene hydroperoxide:



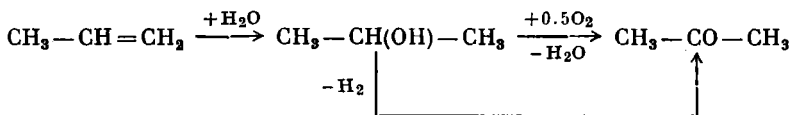
This process has substantial advantages over the sulphonation method.

Acetone, $\text{CH}_3\text{—CO—CH}_3$, is a liquid (b.p. 56.1 °C) which is miscible with water and many organic substances. It is flammable and forms explosive mixtures with air within the concentration limits of 2.2-13.0 percent (by volume). Acetone is extensively employed as a solvent and as an intermediate of organic synthesis. It is used to obtain diphenylolpropane (for the production of epoxy resins and polycarbonates), diacetone alcohol, methyl isobutyl ketone, methyl methacrylate (via acetone cyanohydrin), methyl vinyl ketone and other valuable compounds.

Acetone was originally derived from the products of dry distillation of wood and of the acetone-butyl fermentation of carbohydrates. Synthetic acetone was produced by the gas-phase hydration of acetylene:



and (mainly) by the hydration of olefins followed by the oxidation or dehydrogenation of the resultant alcohols:



The method of combined production of acetone and phenol is the most economical method and in some countries it has superseded the other processes. In other countries the demand for acetone exceeds the capacity of the cumene method, which is why it is additionally produced from propylene.

6.2.2.4. Technology of Production of Phenol and Acetone by the Cumene Process

The production of phenol and acetone by the cumene process involves the steps of preparation of isopropylbenzene (page 264), the synthesis of isopropylbenzene hydroperoxide and its acidic decomposition to phenol and acetone.

separator 3, washed with caustic and again led to oxidation. The still liquid from column 6 contains 70-75 percent of the hydroperoxide and also the oxidation by-products and traces of isopropylbenzene. The hydroperoxide concentration is increased up to 88-92 percent by additional vacuum-fractionation (not shown in the flow diagram) at a residual pressure of ≈ 665 Pa. The next step (the acidic decomposition of the hydroperoxide) is effected in unit 7 by one of the two methods described above.

The final step consists of fractional distillation, which is carried out in various sequences. More often acetone is first distilled off in column 8 under ordinary pressure; then the mixture of high-boiling substances (phenolic resins) left in the still is separated in column 9 at reduced pressure from the more volatile products, including phenol. α -Methylstyrene and residual isopropylbenzene (the hydrocarbon fraction) are distilled off from this fraction in column 10 and in column 11 phenol distills out, an additional amount of phenolic resins being left in the still.

In some plants the hydrocarbon fraction is hydrogenated and recycled to oxidation. This prevents the inhibiting action of α -methylstyrene and allows one to avoid concentrating the hydroperoxide prior to decomposition or only to "strengthen" it. A number of methods have been proposed for the utilization of phenolic resins, including pyrolysis with the formation of an additional amount of phenol.

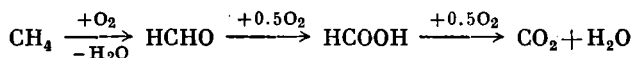
6.2.3. Oxidation of Paraffins

Apart from the above-described oxidation of isobutane and isopentane to hydroperoxides, there are also known the following three processes for the oxidative processing of paraffins:

- (1) oxidation in the gas phase for the production of lower alcohols and aldehydes;
- (2) thermal oxidation in the liquid phase in the presence of boric acid for the synthesis of higher secondary alcohols (C_{10} - C_{20});
- (3) catalytic oxidation in the liquid phase for the manufacture of carboxylic acids; this is the most favoured process.

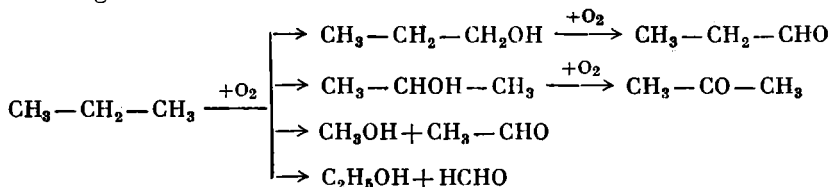
Oxidation of Lower Paraffins in the Gas Phase. The ability of lower paraffins to undergo oxidation depends on the chain length. For example, in the absence of catalysts and at ordinary pressure methane begins to be oxidized at 420°C , ethane at 285°C , and propane at 270°C . As the pressure increases the initial oxidation temperature decreases; for example, methane at 10 MPa reacts with oxygen even at 330°C . Homogeneous initiators (nitrogen oxides, HBr) and also heterogeneous catalysts make it possible to accelerate the process and to effect it at a lower temperature.

The gas-phase oxidation may occur either with retention or with disruption of the carbon chain. Many attempts have been made to develop the process of direct oxidation of methane to formaldehyde, but they have failed because of the relative ease of further oxidation and decomposition of formaldehyde:



Therefore, a satisfactory selectivity with respect to formaldehyde is achieved only with a very low extent of oxidation of methane under the conditions of oxygen deficiency, which can be achieved only with much recycle of the hydrocarbon feed. The method has proved uneconomic.

The gas-phase oxidation of C_3 - C_4 paraffins gives a mixture of alcohols and carbonyl compounds formed either with retention or with degradation of the carbon chain:



The amount of chain degradation products increases with increasing temperature, being equal, for example, to 76 and 98 percent for propane at 250 and 373 °C, respectively. This process has been realized industrially only in the USA and is used for the manufacture of formaldehyde, acetaldehyde, methanol and the so-called mixed solvent, which contains C_2 - C_3 alcohols, acetone and methyl ethyl ketone. The oxidation of C_3 - C_4 paraffins is carried out at 400 °C and with an oxygen deficiency in a hollow adiabatic reactor at a pressure of 0.7-2 MPa. A disadvantage of the process is the complex composition of the mixture, which calls for increased capital investment and energy consumption at the separation step.

Oxidation of Normal Paraffins to Alcohols. The C_{10} - C_{20} alcohols of normal structure are of value as the feedstock for the synthesis of surfactants. The production of these alcohols by the oxidation of soft paraffin wax using the Bashkirov method has been developed and realized industrially in the USSR.

The oxidation is carried out without the aid of catalysts but in the presence of 4-5 percent of boric acid at 165-170 °C in a bubble reactor using air depleted in oxygen (3-4.5 percent by volume of O_2). These conditions encourage the predominant formation of alcohols; the acid reacts with them to form esters which do not undergo further oxidation:



These esters are separated and hydrolyzed by water and the boric acid is recycled to oxidation.

The resultant alcohols formed with the carbon chain remaining intact are chiefly secondary and contain impurities of glycols and ketoalcohols. This fraction is of little value as the feedstock for the production of surfactants, which is why this method of oxidation of paraffins has not found wide application.

Oxidation of Paraffins to Carboxylic Acids. This route to the oxidation of paraffins always involves the disruption of carbon-carbon bonds. The process occurs in the liquid phase—thermally or in the presence of a catalyst at a temperature ranging from 105–120 to 170–200°C. Two routes are used:

(1) oxidation of lower paraffins (C_4 – C_9) predominantly to acetic acid;

(2) oxidation of hard paraffin wax to the so-called synthetic fatty acids (SFA) with a straight chain of carbon atoms (C_{10} – C_{20}), which are the feedstock for the synthesis of surfactants.

Oxidation of C_4 – C_8 Paraffins. The fission of the chain upon oxidation of n -paraffins occurs chiefly across the bonds between secondary carbon atoms. This explains why n -butane mainly gives acetic acid and the by-products formed are methyl ethyl ketone and ethyl acetate:

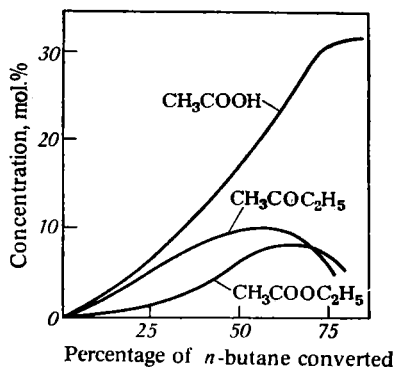
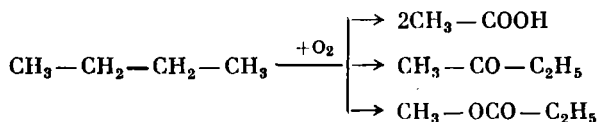


Fig. 6.9. The curves of accumulation of the products of the liquid-phase oxidation of n -butane.

The curves showing the dependence of the content of these compounds in the reaction mass on the degree of conversion of n -butane at 145°C are given in Fig. 6.9 (these curves are also typical of the liquid-phase oxidation of other paraffins). Figure 6.9 shows that the concentration of the ketone passes through a maximum, which is evidence of the ability of the ketone to undergo further oxidation to the acid. The curve of accumulation of ethyl acetate also has a maximum, but it is shifted more strongly to the right than in the case of the ketone. Besides, there have been detected more than a

dozen of other oxidation by-products—alcohols, carbonyl compounds and esters.

The oxidation of *n*-butane is carried out with air in a solution of acetic acid at 160–190 °C and 6 MPa without catalysts or in the presence of cobaltous or manganous salts. The main difficulty in the realization of this process was the complexity of the separation of the multi-component mixture of products formed. In this way acetic acid is produced only in the USA.

The method of oxidation of the light fraction of straight-run gasoline (C_5 – C_8), which is cheaper than *n*-butane, finds an ever

increasing application. This fraction contains a mixture of *n*- and isoparaffins, which complicates the reaction and the composition of the products. These products can, however, be separated into two groups: acids (formic, acetic, propionic and succinic acids) and neutral compounds (alcohols and ketones). The latter are more volatile (as pure compounds or in the form of azeotropic mixtures with water, which is also present in the oxidation products) and this allows them to be separated from the acids and to be returned to oxidation. From the acid fraction there are isolated pure formic, acetic, propionic and succinic acids; their yield from 100 kg of gasoline is, respectively, 20, 70–75, 10–15 and 5–10 kg.

The oxidation of gasoline is effected thermally or using a catalyst at 170–200 °C and 5 MPa. Since the end products are stable to further oxidation, the reactor used is a simple bubble-cap column; the heat evolved is removed by the evaporation of gasoline and neutral oxidation products (Fig. 6.10). The reaction mixture is led to column 2, where the unconverted gasoline and the neutral substances are distilled off and returned to the reactor. The still liquid from this column is sent to the acid recovery unit.

The success of the process described has been due not only to the simplification of the product separation step but also to the efficient heat utilization system. The residual air together with the vapours of the organic compounds from the top of the reactor passes into waste-heat boiler 3, where steam of the appropriate pressure is generated. The heat of the gas is then used in heat exchanger 4 for heating the water and the pressure of the gas in expander 6 is

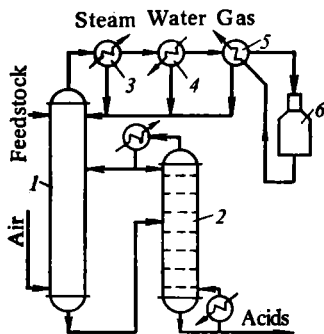


Fig. 6.10. Flow diagram of oxidation of the light fraction of straight-run gasoline:

1—reaction column; 2—fractionating column; 3—waste-heat boiler; 4—heat exchanger; 5—cooler; 6—expander.

transformed into the cold, which is used in cooler 5 to condense out the residual gasoline from the gas. The mixed condensate is returned to the oxidation column.

Oxidation of Hard Paraffin in SFA. Because of the large chain length very complex mixtures of products are obtained. The attack on the hydrocarbon molecule occurs with equal probability at any of the secondary carbon atoms and the chain is broken at any carbon-carbon bond. As a result, partially oxidized products are formed — ketones having the same number of carbon atoms and alcohols of differing structure. Upon oxidation of the hard C_{30} paraffin the acids formed consist of 60 percent of the C_{10} - C_{20} fraction; there are also formed C_1 - C_4 and C_5 - C_9 acids and higher acids (with more than 20 carbon atoms). A specific feature of higher carboxylic acids is their ability to be oxidized to hydroxy-acids and lactones, and ketonic and dicarboxylic acids. The impurity of the last name compounds lowers the quality of the end acids, which is why the degree of conversion of the paraffin feed and the temperature of the process have to be limited.

The curves of the variation of the acid, ester and carbonyl numbers, which characterize the content of acids, esters and carbonyl compounds, respectively, are shown in Fig. 6.11. The concentration of ketones passes through a maximum, and for esters the maximum does not yet appear with the degree of conversion of the paraffin being not high. The increase of the acid number is slowed down, beginning with 70-80 mg KOH per 1 g.

When a paraffin consisting of hydrocarbons with an average number of carbon atoms (about 30) is oxidized, the yield of carboxylic acids amounts to 80 percent. The resultant mixture of acids of differing molecular mass has the following composition (in percent):

C_1 - C_4	5-10	C_{10} - C_{18}	25-28
C_5 - C_6	3-5	C_{17} - C_{20}	15-20
C_7 - C_9	8-10	$>C_{20}$	20-25

For soapmaking use is made of the C_{10} - C_{20} fraction: the C_{10} - C_{16} fraction goes for the production of toilet soap and the C_{17} - C_{20} fraction

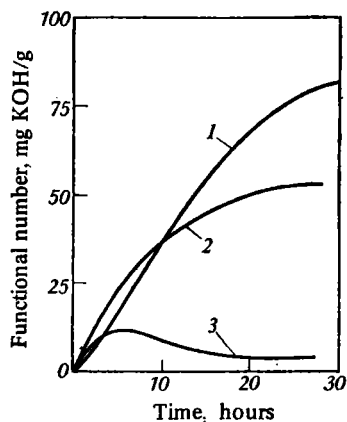


Fig. 6.11. Variation of the acid (1), ester (2) and carbonyl (3) numbers of the reaction mass during the catalytic oxidation of a paraffin.

for household soap. The lower acids that are insoluble in water (C_7 - C_9) are used for the production of the corresponding alcohols (by hydrogenation) and also for the manufacture of plasticizers and lubricating oils (in the form of esters with polyhydric alcohols). The lower water-soluble acids (C_1 - C_4) are not used, being lost with the wash waters. The higher acids ($>C_{20}$) are partly used for the manufacture of household soap. The residue from distillation also contains dicarboxylic acids.

Of the other products formed in the oxidation of paraffins, alcohols are of considerable interest. They can be obtained (after the saponification of esters and the extraction of acids by aqueous alkalis) in the form of the esters of boric acid, the amount of these alcohols amounting to 8-10 percent based on the paraffin feedstock. The alcohols contain 8-26 carbon atoms in the molecule and are chiefly (by 65-75 percent) primary alcohols. They are successfully used for the synthesis of surfactants of the alkyl sulphate type.

The oxidation of paraffins can be carried out at 150-170 °C without the aid of catalysts, but in this case low-quality acids are obtained. The process occurs more selectively in the presence of catalysts added to the paraffin in the form of aqueous solutions of potassium permanganate, certain manganese salts, manganese peroxide or a mixture resulting from the recovery of manganese from the oxygenated compounds. The compounds indicated are insoluble in the paraffin, which is why a temperature of 125-130 °C is maintained initially (for 2 hours) in order to complete the formation of a homogeneous catalyst (the manganese salts of higher carboxylic acids). It has been found that the activity of the catalyst increases if it contains sodium (and especially potassium) hydroxide, which is converted upon oxidation to the corresponding salt. The optimum ratio of Mn^{2+} to K^+ is $\approx 1 : 1$.

The rate of the liquid-phase oxidation of the paraffin depends on many factors—the concentration of the catalyst, temperature, the partial oxygen pressure, the linear velocity of the oxidizing gas and even on the size of openings through which the gas bubbles into the reaction mass. In industrial practice, the catalyst concentration is limited to 0.2-0.3 percent (by weight) of $KMnO_4$ [about 0.10 percent (by weight) based on Mn]. As the temperature is raised the rate of the process increases. For example, the same degree of conversion (30-35 percent) is achieved at 80 °C in 110 hours, at 100 °C in 38 hours, and at 110 °C in 24 hours. With increasing temperature the reaction may be switched over into the diffusional region, as a result of which the hydrodynamic conditions in the reactor become very important. The factors indicated have an effect not only on the reaction velocity but also on the composition of the compounds formed, on the yield and quality of the major fraction of higher carboxylic acids. For instance, in the transient or diffusion regime

the amount of overoxidized compounds increases considerably and the quality of the end acids is lowered.

A process of the liquid-phase catalytic oxidation of paraffins has been developed with all these considerations being taken into account; the process has the following indices: the degree of conversion of the paraffin does not exceed 30-35 percent (which corresponds to the acid number of ≈ 70 mg KOH per 1 g of the oxygenated compound);

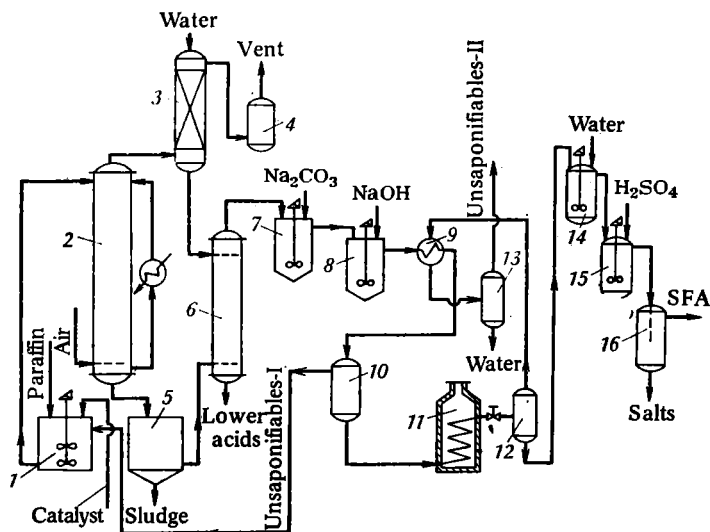


Fig. 6.12. Flow diagram of the oxidation of a hard paraffin:

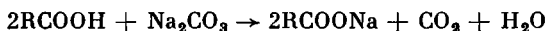
1—mixer; 2—oxidation column; 3, 6—scrubbers; 4—combustion chamber; 5—settler; 7, 8—saponifiers; 9—heat exchanger; 10—autoclave; 11—tubular furnace; 12, 13, 16—separators; 14, 15—stirred units.

when the process is started, the temperature is maintained at 125-130 °C and then it is lowered to 105-110 °C; the oxidation is carried out at atmospheric pressure, the air being admitted into the reaction bubble-cap column through the distribution arrangements with a large number of small openings (1-2 mm). The use of more than a twofold excess of air provides a vigorous agitation of the reaction mass. Under these conditions and with the amounts of the manganese catalyst indicated above the paraffin oxidation takes 15-20 hours.

The flow diagram of the process is given in Fig. 6.12. Fresh paraffin and the product from the separation stage (so-called unsaponifiables-I) in the ratio of 1 : 2 and also the catalyst are mixed in unit 1. The blend is passed for oxidation to column 2, which operates batchwise. This column is constructed of aluminium or a special grade of steel, is fitted with a jacket for heating or cooling, an external cooler for the removal of heat and a distribution arrangement for

the admittance of air. The gas from the top of the column is washed with water in column 3 for the absorption of lower acids, purified from the impurities by combustion in furnace 4 and discharged into the atmosphere.

Upon completion of the reaction the oxygenated compound is cooled down to 80-90 °C and run to settling tank 5, where the catalyst slurry is separated (the catalyst can be regenerated from it). In column 6 the oxygenated compound is washed off from the lower water-soluble acids with the water flowing down from column 3. It is then treated with an aqueous solution of soda ash in saponifier 7, the free acids being converted into the salts:



and with an aqueous solution of caustic in saponifier 8, where the hydrolysis of the esters and lactones takes place:



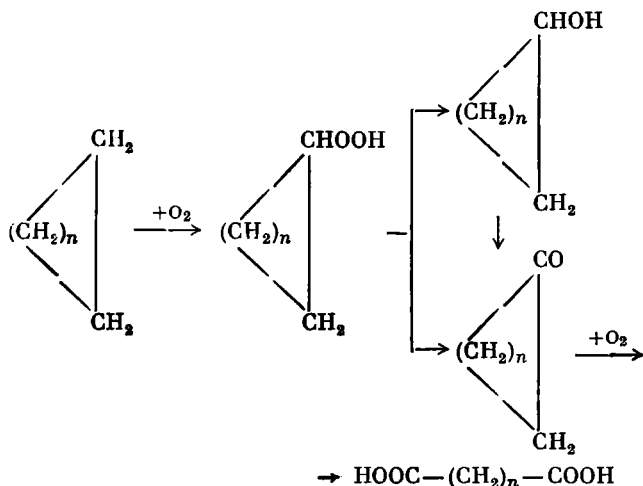
The saponification of the difficultly hydrolyzable compounds is completed at a pressure of 2 MPa in heat exchanger 9 and in autoclave 10 at 180 °C. In the autoclave the aqueous solution of the salts of the carboxylic acids are separated from the unsaponifiables-I, which are returned for the preparation of the charge. But the soap from autoclave 10 still contains unsaponifiables-I; they have to be distilled off at a high temperature, which contributes to the improvement of the quality of the acids. For this purpose, the soap is heated in tubular furnace 11 up to 320-340 °C and the mixture is throttled to separate the vapours of the volatile compounds in separator 12. After the condensation of the vapours in heat exchanger 9 the condensate is separated in separator 13 into an aqueous and an organic phase; the latter consists of the so-called unsaponifiables-II. They are returned for oxidation or the alcohols are recovered from them.

The soap from separator 12 is dissolved in water in mixer 14 and treated with sulphuric acid in unit 15, following which the solution of salts is separated from the free acids in separator 16. These acids are distilled in several stills equipped with fractionating columns (not shown in the flow diagram) at 1.33 Pa with the acid fractions $\text{C}_5\text{-C}_6$, $\text{C}_7\text{-C}_9$, $\text{C}_{10}\text{-C}_{16}$ and $\text{C}_{17}\text{-C}_{20}$ being distilled off. The residue is a mixture of acids higher than C_{20} and dicarboxylic acids.

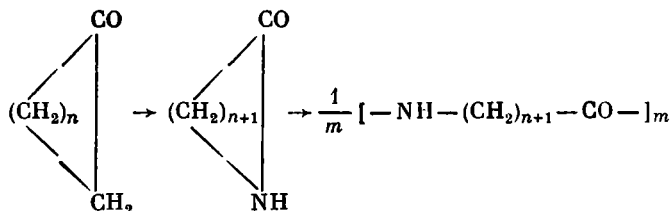
The above-described process of oxidation of hard paraffin to higher fatty acids has substantial disadvantages: a low capacity, the batch-wise operation and the formation of a large number of by-products. The process is being improved by way of its intensification, the development of a continuous operation and by searching for the possibility of the maximum utilization of the wastes (lower carboxylic acids, dicarboxylic acids, etc.).

6.2.4. Oxidation of Naphthenes and Their Derivatives

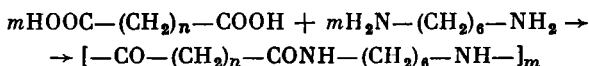
The oxidation of naphthenic hydrocarbons (cyclanes) is similar in many respects to the oxidation of paraffins. In the gas-phase process the ring undergoes a strong degradation, but at a moderate oxidation temperature in the liquid phase there is observed an ordinary sequence in the formation of the products:



The practical value of this process is that it leads to the formation of the corresponding ketones (cyclanones) with C_5 - C_{12} rings and α,ω -dicarboxylic acids with 5-12 carbon atoms. These compounds are used as the feedstock for the production of the most important polyamides and polyamide fibres (capron, nylon). For this purpose, ketones are converted to lactams, which are then polymerized:



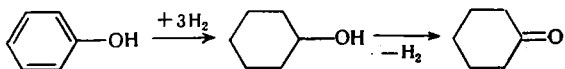
and the dicarboxylic acids are condensed with diamines, mostly with hexamethylenediamine:



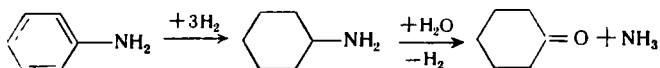
Besides, the dicarboxylic acids serve as the feedstock for the synthesis of valuable plasticizers—their esters with C_7 - C_9 alcohols.

6.2.4.1. Cyclanones and Dicarboxylic Acids

Of the most practical importance among the cyclanones is *cyclohexanone (anone)*  which is a liquid (b.p. 157 °C) soluble in water to a limited extent. It is used for the production of caprolactam and the synthetic fibre capron (nylon-6), as a solvent and a substitute for camphor. The principal method of cyclohexanone production consists of the oxidation of cyclohexane; the co-product cyclohexanol (anol) can also be converted to a ketone by way of dehydrogenation. This reaction formed the basis of the first industrially realized methods of synthesis of cyclohexanone—from phenol which is preliminarily hydrogenated to cyclohexanol:



Another method of cyclohexanone synthesis has also found application, though to a limited extent—from aniline via cyclohexylamine:



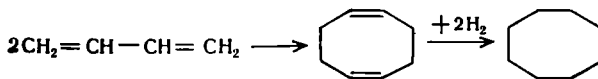
All these processes are closely associated with the production of caprolactam and are the steps of a single technological process. They are all based on the benzene feedstock; because of the lesser number of steps and the consumption of a lower quantity of the feedstock the method of cyclohexanone production by the oxidation of cyclohexane is preferable.

The oxidation of cyclohexane is also carried out to produce the most important of the aliphatic dicarboxylic acids—*adipic acid*, $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$. Adipic acid is a colourless crystalline substance (m.p. 152 °C), which is but slightly soluble in cold water. It is used for the synthesis of the fibre nylon 6,6 and plasticizers.

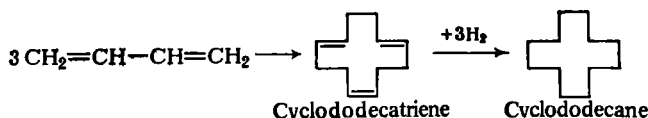
The problem of the production of other cyclanones and dicarboxylic acids is associated with the availability of the corresponding naphthenic hydrocarbons. Cyclopentane can be obtained by the hydrogenation of cyclopentadiene and cyclopentene, which are present in the products of petroleum processing. Cyclopentane is oxidized to

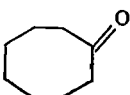
form *cyclopentanone*,  and *glutaric acid*, $\text{HOOC}-(\text{CH}_2)_3-\text{COOH}$. The latter is also a by-product in the manufacture of adipic acid. The other cyclanes are synthetic products; among these only

cyclooctane and cyclododecane are relatively available. They are made by the cyclooligomerization of butadiene followed by the hydrogenation of the cycloolefins formed:



The cyclodimerization of butadiene can, for example, be carried out over a metal-complex catalyst, $(\text{C}_6\text{H}_5\text{O})_3\text{P}\cdot\text{Ni}(\text{CO})_4$, at 165°C and ≈ 4 MPa in a solvent with a yield of ≈ 70 percent. The cyclotrimerization of butadiene is effected using the Ziegler catalyst $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}\cdot\text{TiCl}_4$ at $50\text{--}60^\circ\text{C}$ in a solvent at ordinary pressure with a yield of up to 90–95 percent.

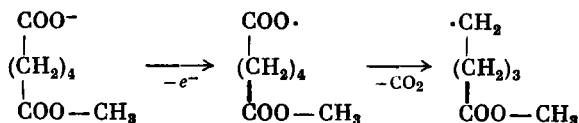


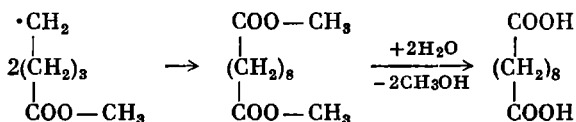
The oxidation of cyclooctane gives *cyclooctanone*  and

suberic acid (octanedioic acid), $\text{HOOC}-(\text{CH}_2)_6-\text{COOH}$, and cyclododecane when oxidized gives *cyclododecanone* and also *dodecanedicarboxylic acid*, $\text{HOOC}-(\text{CH}_2)_{10}-\text{COOH}$, which is also known as 1,10-decanedicarboxylic acid.

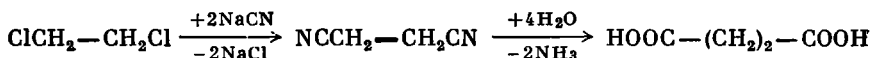
The other naphthenes are not readily available, which is why the higher dicarboxylic acids are produced by various methods. Of these acids, only *azelaic acid* (C_9) and *sebacic acid* (C_{10}) are of considerable interest. One of the general methods of their production consists of the oxidation or alkaline decomposition of the higher unsaturated acids, their esters or natural oils that contain these esters (castor oil, etc.).

Of interest is the synthesis of sebacic acid by the electrochemical dimerization of adipic acid. When the salt of the monoester of adipic acid in an alcoholic solution is subjected to electrolysis, a radical is formed on the anode, which as in the ordinary Kolbe synthesis, splits off carbon dioxide and is dimerized to the diester of sebacic acid:



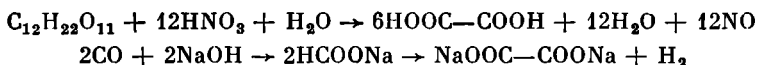


Here it is also expedient to consider the synthesis of lower dicarboxylic acids. *Succinic acid*, $\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$, has already been encountered as a by-product of the oxidation of C_5 - C_8 paraffins (page 410). It can also be produced from 1,2-dichloroethane via the dinitrile:



Succinic acid is also formed as a by-product in the manufacture of adipic acid.

Oxalic acid, $\text{HOOC}-\text{COOH}$, is also formed in the production of adipic acid. Besides, it can be obtained by the oxidation of carbohydrates, ethylene glycol, ethylene and wood and synthesized from carbon monoxide:



6.2.4.2. Oxidation of Naphthenes to Alcohols and Ketones

The oxidation of naphthenes to a mixture of an alcohol and a ketone is one of the two most important routes for the processing of these hydrocarbons. It can be effected with air in the liquid phase at 120-200 °C, either thermally or in the presence of catalysts under pressure, which maintains the liquid state of the reaction mixture. The usual alcohol/ketone ratio is 2 : 3, but the reaction products also contain the hydroperoxide, glycols, ketoalcohols, diketones, carboxylic acids, lactones and esters. The amount of the hydroperoxide increases with increasing ring size and with decreasing temperature and catalyst concentration.

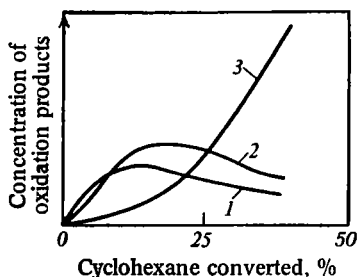


Fig. 6.13. The curves of accumulation of the oxidation products of cyclohexane:

1—cyclohexanol; 2—cyclohexanone; 3—carboxylic acids.

As shown in Fig. 6.13, the alcohol and ketone, being the intermediates of the oxidation reaction, are accumulated according to a curve with a maximum; a satisfactory yield of these compounds can be obtained only with a low degree of conversion of the naphthene.

Catalytic Oxidation. This reaction gives the best results in the oxidation of C_5 - C_6 naphthenes; in this way cyclohexanol and cyclohexanone are produced from cyclohexane. The most effective catalysts are cobalt salts at 120-160 °C and 1-2 MBa. The selectivity with respect to the alcohol-ketone mixture depends very strongly on the degree of conversion of cyclohexane, which has to be maintained at the level of 4-5 percent in order to eventually attain a yield of anol and anone amounting to ≈ 80 percent. For the same reason, the oxidation process is carried out in a cascade of 3-4 bubble-cap columns.

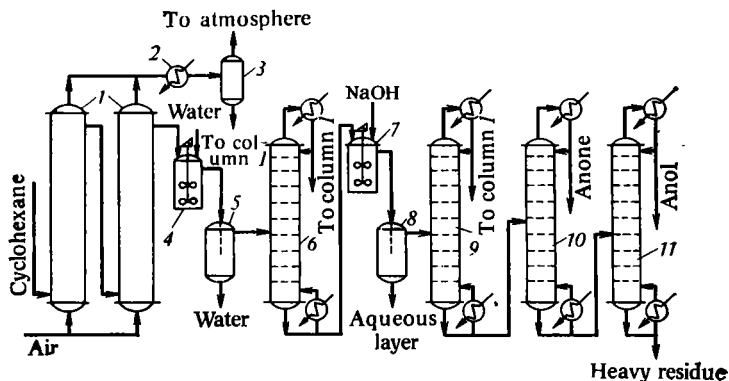


Fig. 6.14. Flow diagram of the oxidation of cyclohexane to a mixture of cyclohexanol (anol) and cyclohexanone (anone):

1—oxidation columns; 2—cooler; 3, 5, 8—separators; 4, 7—mixers; 6, 9, 10, 11—fractionating columns.

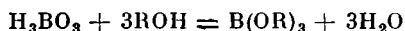
A simplified flow diagram of the process is shown in Fig. 6.14. The oxidation is effected in a cascade of bubble columns 1 with a successive overflow of the liquid and supply of air to each of the columns. The heat of the reaction is removed by the evaporation of excess cyclohexane, which is condensed in cooler 2 used for all the columns, separated from the gas in separator 3 and passed to the cyclohexane recirculation line. The oxygenated compounds from the last column is washed with water (to recover the lower acids) in mixer 4 and separated from the aqueous layer in separator 5. Then, the major proportion of cyclohexane is distilled off from the oxygenated mixture in column 6; the amount left in the still should be such as to prevent the hydroperoxide concentration from exceeding the safe level (3-4 percent). The still liquid is then treated upon heating in a cascade of stirred units 7 (only one unit is shown in the flow diagram) with aqueous caustic. Here the esters and lactones are saponified and the hydroperoxide is decomposed. The organic layer is separated from the aqueous layer in separator 8 and the cyclohexane is distilled from it in column 9. The cyclohexane from columns 6 and 9 and from separator 3 is returned to oxidation.

The still liquid of column 9 contains cyclohexanol, cyclohexanone and neutral by-products. The cyclohexanone distills out in column 10 and the cyclohexanol in column 11. If the major product is only cyclohexanone, it is necessary that the flow diagram be provided with a cyclohexanol dehydrogenation unit.

Thermal Oxidation of Cycloalkanes in the Presence of Boric Acid.

The above-described process of catalytic oxidation of cycloalkanes is characterized by a low selectivity even at a low degree of conversion of the feedstock. This shortcoming becomes especially important in the oxidation of C_8 and C_{12} cycloalkanes when the catalytic oxidation proceeds even less selectively and the starting hydrocarbons are expensive as compared to cyclohexane. This has led to the development of other, more selective oxidation processes.

For example, it has been suggested that C_8 and C_{12} cycloalkanes be oxidized to hydroperoxides with their decomposition by alkali to an alcohol-ketone mixture. A more efficient method is the thermal oxidation with air depleted in oxygen (to a concentration of 3-4 percent O_2). As has already been shown (page 393) these conditions, just as in the case of the oxidation of paraffins (page 409), encourage the predominant formation of alcohol as compared with the ketone. If the process is carried out in the presence of boric acid, the acid will bind the alcohols into esters:



which do not undergo further oxidation. This route prevents to a considerable extent a stronger oxidation and even at a relatively high degree of conversion there is attained a relatively high selectivity: with this method of oxidation of cyclododecane at its 30-35 percent conversion the selectivity with respect to the alcohol-ketone mixture amounts to 90 percent, the alcohol-ketone ratio reaching 9 : 1.

The flow diagram of the thermal oxidation of cyclododecane in the presence of boric acid is shown in Fig. 6.15. Boric acid and cyclododecane are introduced into mixer 1, where a suspension of these compounds is prepared. It flows down into column 2, where at 150-200 °C the oxidation is effected with air depleted in oxygen due to the recirculation of part of the off-gas after cooler 3. The oxygenated mixture is passed to column 4 for the distillation of the unconverted hydrocarbon; the compounds left in the still of this column are the esters of boric acid, ketone and oxidation by-products. They are pumped into hydrolyzer 5, where the hydrolysis of the esters of boric acid takes place with water being supplied and on stirring. In separator 6 the organic layer is separated from the aqueous layer and is sent for fractionation with the recovery of the alcohol, ketone and heavy residue. The aqueous layer is subjected to treatment to regenerate H_3BO_3 (not shown in the flow diagram):

the acid is concentrated by evaporation, crystallized, filtered off and returned to unit 1.

A disadvantage of this process is the use of additional units for the recirculation of boric acid; it is in the solid state, which com-

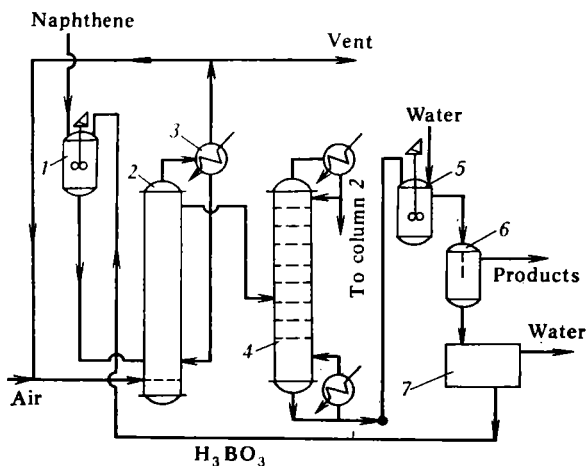


Fig. 6.15. Flow diagram of the oxidation of cyclododecane in the presence of boric acid:

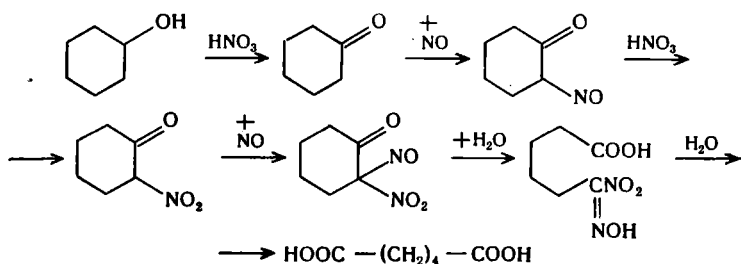
1—mixer; 2—oxidation column; 3—cooler; 4—fractionating column; 5—hydrolyzer; 6—separator; 7—unit for recovery of boric acid.

plicates the transfer of the streams and the continuous operation of the process. This process has, however, been operated in some countries for the oxidation of cyclohexane.

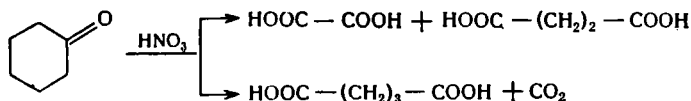
6.2.4.3. Production of Dicarboxylic Acids

As can be seen from Fig. 6.13, in the sequential development of the reactions of oxidation of cycloalkanes the yield of dicarboxylic acids increases steadily and it would seem that the acids could be produced in this way by carrying out a direct one-step oxidation of cycloalkanes. In reality, however, because of the formation of many by-products and of the combustion to CO_2 the oxidation selectivity with respect to the major dicarboxylic acid does not exceed 40-50 percent. A two-stage process has therefore been realized industrially, which consists of the initial oxidation of a cycloalkane with air to an alcohol-ketone mixture and of their subsequent oxidation with nitric acid to the dicarboxylic acid. Often, only the alcohol is sent to the second stage and the ketone goes to the synthesis of a lactam.

The Second Step of the Two-Stage Oxidation. The second step is one of the most significant example of the use of nitric acid as an oxidizing agent; the optimum concentration of the acid for this case is 40-60 percent. The alcohol is first oxidized to the ketone, this being followed by the nitrosation reaction, the rearrangement of the nitroso compounds to oximes, the hydrolysis of the oximes to ketonic compounds, etc. It is presumed that adipic acid is formed from cyclohexanol via the following intermediate steps:



The side reactions involved lead to the formation of oxalic, succinic and glutaric acids:



and, as a result of the splitting-off of CO and CO₂, a monocarboxylic (valeric) acid, C₄H₉COOH, is formed at one of the intermediate steps. The consumption of nitric acid on oxidation is ≈ 2.3 moles per 1 mole of cyclohexanol, the corresponding amount of oxides of nitrogen being formed.

The yield of adipic acid increases when the oxidation is carried out in a two-temperature regime: at 60-80 °C in the first step and at 100-120 °C in the second (this is explained by the fact that the formation of intermediate products of the synthesis of adipic acid proceeds with a lower activation energy than the intermediate steps of formation of by-products, whereas the hydrolysis of these compounds to adipic acid requires an elevated temperature). A positive effect is also provided by a copper-vanadium catalyst added in the form of a copper oxide and ammonium metavanadate (in an amount of ≈ 0.07 percent of each of the components based on the cyclohexanol used). Copper binds nitrogen oxides into complexes and the vanadium compounds accelerate the major reaction and increase the yield of adipic acid up to 90-95 percent.

Such a two-temperature regime is effected in two successively arranged reactors operating at different temperatures. The first reactor is a stirred or a flow-circulation unit, since the reaction is strongly exothermic and a direct contact of cyclohexanol with 60-percent HNO_3 may result in an explosion. The economic success of the process depends largely on the utilization of the oxides of nitrogen formed; they are converted to nitric acid, thus reducing its consumption.

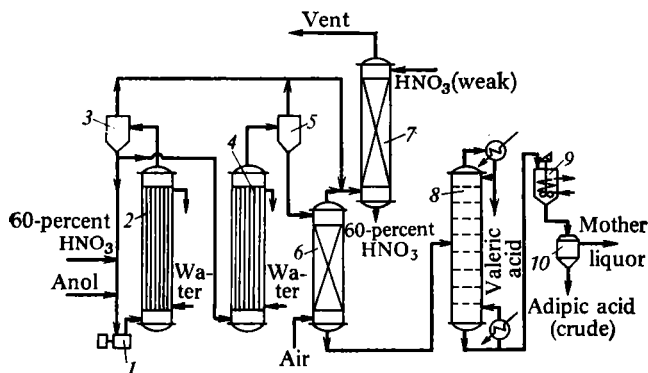


Fig. 6.16. Flow diagram of the oxidation of cyclohexanol to adipic acid:
1—pump; 2, 4—reactors; 3, 5—separators; 6, 7—scrubbers; 8—vacuum fractionator; 9—crystallization unit; 10—centrifuge.

tion to a minimum. In order to improve the conditions of absorption of nitrogen oxides, the oxidation is carried out at elevated pressure (0.3-0.5 MPa).

A simplified flow diagram of the production of adipic acid from cyclohexanol is given in Fig. 6.16. The anol and fresh 60-percent nitric acid (in a twofold amount with respect to the stoichiometric amount and with addition of a copper-vanadium catalyst) is introduced into the suction line of pump 1, where they are diluted with a large volume of the circulating oxygenated compound and then led to water-cooled tubular reactor 2.

In reactor 2, the major conversions take place at 60-80 °C and 0.3-0.5 MPa. The oxygenated mixture from the first step leaves the top of reactor 2 and is freed in separator 3 from the nitrogen oxides formed, following which the major proportion is recycled, the remainder being led to reactor 4 of the second oxidation step. The oxygenated mixture from the second oxidation step is separated from nitrogen oxides in separator 5 and is additionally purged with air in scrubber 6. The purge gas together with the nitrogen oxides leaves separators 3 and 5 and is run to scrubber 7 refluxed with nitric acid, which is "strengthened" to the concentration required for oxidation

(60 percent). The gas leaving scrubber 7 is subjected to purification from toxic substances and is discharged into the atmosphere.

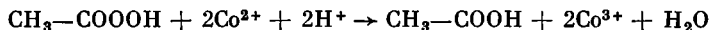
The oxygenated mixture from scrubber 6 is sent to vacuum-fractionation column 8, where valeric acid is distilled off. The still liquid of column 8 is cooled in crystallizer 9, the precipitated crystals of adipic acid are separated from the mother liquor on centrifuge 10. The adipic acid is subjected to additional purification by crystallization.

The mother liquor is a mixture of oxalic, succinic and glutaric acids and part of adipic acid, which are all dissolved in a weak nitric acid solution. A number of methods have been developed for the processing of the mother liquor with a view to regenerating the nitric and dicarboxylic acids. The mother liquor is first concentrated by evaporation and a weak nitric acid is obtained, which is then sent for "strengthening". The dicarboxylic acids can then be isolated by fractional crystallization, extraction, conversion to esters, etc.

The above-described two-step process for the production of adipic acid involves the oxidation of cyclohexane with air and the oxidation of cyclohexanol by nitric acid and requires the corresponding units for the separation and purification of the products; this is associated with increased capital investment. At the same time, the one-step oxidation of cyclohexane in the oxygenated medium gives a low yield of adipic acid.

One-Step Oxidation of Cyclohexane to Adipic Acid. A different one-step process has recently been worked out, which provides much better results. The air oxidation of cyclohexane is effected in a solution of acetic acid at 80-100 °C in the presence of a catalyst (cobalt acetate) promoted with acetaldehyde or methyl ethyl ketone.

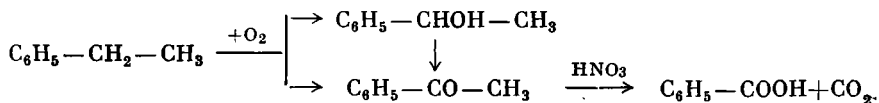
The role of the promoter is presumably as follows: the peracetic acid resulting from its oxidation maintains the cobalt in the trivalent state:



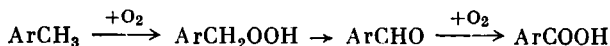
This form of the catalyst is capable of directly oxidizing cyclohexane or intermediate products of its oxidation, which proceeds more selectively than the usual radical-chain process. It has been reported that at 80-90 percent conversion of cyclohexane the selectivity with respect to adipic acid is 70-75 percent. The oxidation is carried out in a bubble column; the unconverted cyclohexane, acetic acid and the water formed are then distilled off from the reaction mass. The water is withdrawn from the system and the cyclohexane and acetic acid are returned to oxidation. In the next separation unit, the by-products are distilled off and the catalyst is regenerated; the adipic acid is sent to the purification unit.

6.2.5. Oxidation of Methylbenzenes to Aromatic Acids

We have already encountered the oxidation of ethyl- and isopropylbenzenes to the corresponding hydroperoxides (page 397). If the process is catalyzed by polyvalent metal salts the products of the oxidation of these alkylbenzenes by molecular oxygen are carbinols and acetophenone, and the carboxylic acids are obtained under special conditions or by the oxidation with nitric acid:

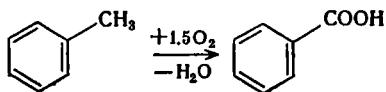


Therefore, the most suitable starting compounds for the synthesis of aromatic acids are the methyl derivatives of benzene, whose radical-chain oxidation proceeds through the primary hydroperoxide and aldehyde step:



6.2.5.1. Aromatic Acids Produced by Liquid-Phase Oxidation

Benzoic acid, $\text{C}_6\text{H}_5-\text{COOH}$, a crystalline substance (m.p. 122 °C), can be obtained by the oxidation of various monoalkylbenzenes, but in practice use is made of the most available compound—toluene:

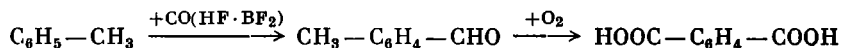


Benzoic acid has only recently become important in basic organic and petrochemical synthesis; this has been favoured by the availability of excessive reserves of toluene. A new method of producing phenol from benzoic acid has been described earlier (page 404). Besides, there is a method for the processing of benzoic acid to caprolactam (page 609) and also to aromatic dicarboxylic acids (page 426).

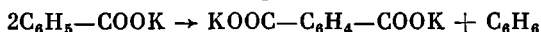
Terephthalic acid, $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$, is also a crystalline sub-

stance (m.p. 300 °C; sublimes). As compared with benzoic acid and its isomeric dicarboxylic acids, terephthalic acid is practically insoluble in water and in most organic solvents. Terephthalic acid and its dimethyl ester (dimethylterephthalate) play an important role in the production of the synthetic fibre lavsan (Terylene)—the product of its polycondensation with ethylene glycol. Terephtha-

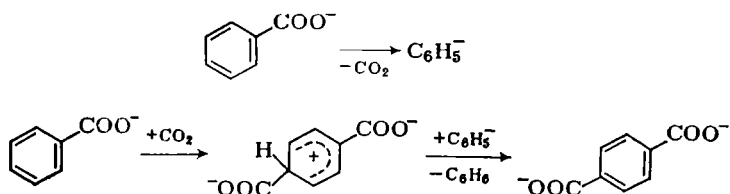
lic acid is produced by starting with *p*-xylene. Since *p*-xylene is relatively expensive, a number of other methods for synthesizing terephthalic acid from more available toluene have been proposed. One method consists of the preparation of *p*-toluylaldehyde and its oxidation to the acid:



In another method, the salts of aromatic acids are subjected to a disproportionation reaction at 400-450 °C in the presence of a catalyst (the carbonate, oxide or organic salts of cadmium):

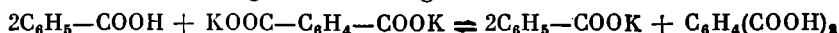


It has been found by investigations in the atmosphere of labeled carbon dioxide that these processes involve the liberation of CO_2 and the carboxylation of the aromatic ring, which is favoured by the positive inductive effect of the carboxylate ion:

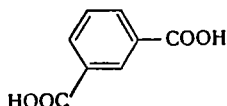


For this reason, the disproportionation proceeds more successfully under pressure of CO_2 (0.3-1 MPa).

Terephthalic acid can be produced in this way from toluene via benzoic acid and its salt, but the original variant of the process did not become popular because of the following two main disadvantages: the mixture is in the solid state and is inconvenient to transfer and complicates the other operations, and the consumption of caustic (and a mineral acid for the recovery of free terephthalic acid) is significant; also, potassium sulphate is formed as a difficultly usable waste. The elimination of these disadvantages has been recently reported: the process is carried out in a suspension of salts in dimethylterephthalate (which is easy to handle), and in order to obtain potassium benzoate and to recover free terephthalic acid, use is made of the following salt-exchange reaction:

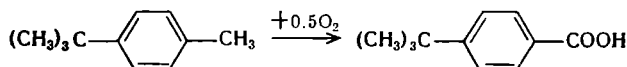


Isophthalic acid (*m*-bensenedicarboxylic acid)



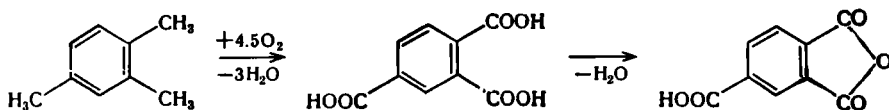
is used for the production of polyesters. It is made in the same way as terephthalic acid—by the liquid-phase oxidation of *m*-xylene.

p-*tert*-Alkylbenzoic acids, especially *p*-*tert*-butylbenzoic acid, made by the oxidation of *p*-*tert*-butyltoluene:

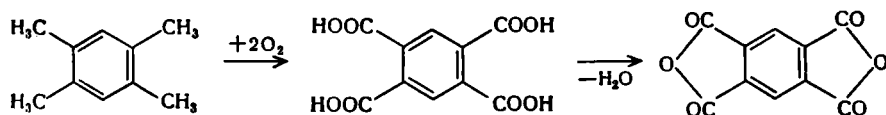


is used for the synthesis of valuable oil-soluble alkyd resins.

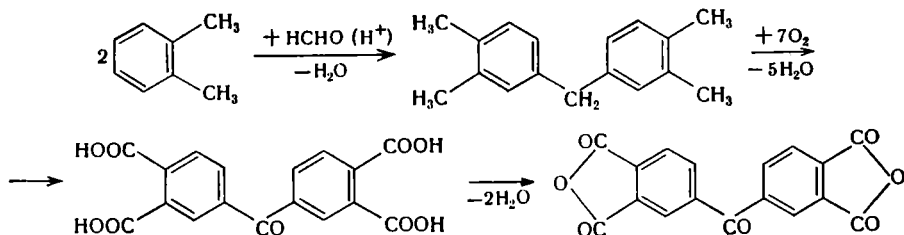
Aromatic polycarboxylic acids have assumed importance in recent years as the starting compounds for the manufacture of thermally stable polymers. *Trimellitic acid* (1,2,4-benzenetricarboxylic acid) and its monoanhydride are formed, like aromatic dicarboxylic acids, upon oxidation of pseudocumene:



Pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) and its dianhydride are made in an analogous way by the liquid-phase oxidation of durene:



Benzophenonetetracarboxylic acid and its dianhydride are produced from *o*-xylene by means of the following conversions, including a liquid-phase oxidation step:

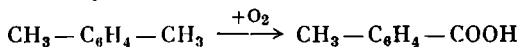


Of interest are also diphenylsulphonetetracarboxylic acid and its dianhydride, naphthalenedicarboxylic acids, naphthalic acid and its anhydride (from acenaphthene) and nitrobenzoic acid (from nitrotoluene).

6.2.5.2. Oxidation of Methylbenzenes in the Medium of the Reagents

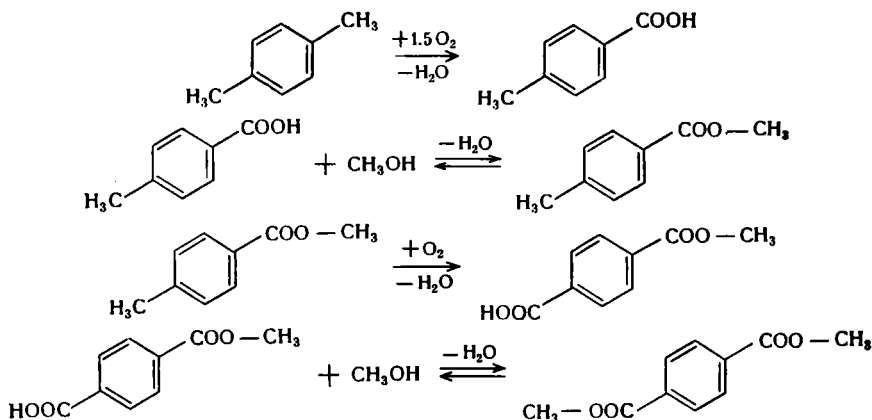
The traditional method of oxidation in the liquid phase of the reactants is also employed for aromatic compounds; the most effective catalysts for this process are soluble cobalt salts. The oxidation is effected with air under pressure; the pressure is required to maintain the liquid state of the reaction mixture. Aromatic acids are stable to further oxidation, and therefore a simple bubble column (in which the heat is removed by any of the existing means; see Fig. 6.5a and b, page 396) may be used as the reactor for a continuous oxidation process.

Whereas toluene is oxidized to benzoic acid in a sufficiently simple way and under mild conditions (at 100-150 °C and a low pressure), the oxidation of xylenes and polymethylbenzenes by molecular oxygen in the presence of salt catalysts is usually completed by the formation of the monocarboxylic acid only. For example, *m*-toluic acid is formed from *p*-xylene and *m*-toluic acid from *m*-xylene, etc.:



This is accounted for by the fact that the carboxyl group that appears deactivates strongly the methyl group left, rendering it incapable of further oxidation. Under more severe conditions (260-280 °C and ≈ 7 MPa) the second methyl group can also be oxidized, but the yield of the dicarboxylic acid will be only 40-60 percent.

It has, however, been observed that the transformation of the carboxyl group to the ester group eliminates the deactivating action of the carboxyl group. This has been used as the basis for development of a four-step process for the production of dimethylterephthalate, which involves the oxidation of *p*-xylene to *p*-toluic acid, the esterification of the latter with methyl alcohol, the oxidation of the ester of *p*-toluic acid to the monoester of terephthalic acid and its esterification to dimethylterephthalate:



In the production of polycarboxylic acids (trimellitic and pyromellitic acids) the number of steps and the difficulties of the separation of the products increase. It has therefore been suggested that the oxidation be initially carried out with air and the process be completed under the action of nitric acid.

Typical curves of accumulation of reaction products for the oxidation of the methyl groups of alkylaromatic compounds are shown in Fig. 6.17. It is seen that the concentration of the aldehyde passes through a maximum. At 50-60 percent conversion of the hydrocarbon the oxidation is retarded, this being presumably associated not only with a decrease in the hydrocarbon concentration but also with the effect of the products formed. The higher the temperature, the greater the degree of conversion at which the process is retarded. This determines the optimum degree of conversion in the liquid-phase oxidation of the side chains of alkylaromatic compounds. After the acid is separated the unconverted hydrocarbon and intermediates are again returned to oxidation.

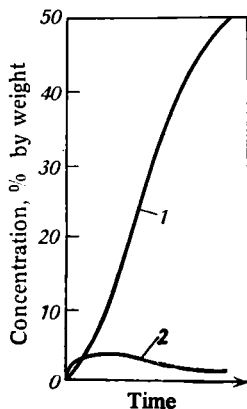


Fig. 6.17. The curves of accumulation of the oxidation products of toluene: 1—benzoic acid; 2—benzaldehyde.

The catalyst in the form of a metal salt soluble in the hydrocarbon (resinate, cobalt naphthenate or the salt of the same acid formed in the oxidation reaction) is used in an amount of 0.05-0.2 percent. The temperature required for the attainment of a high oxidation velocity is usually in the range of 120-200 °C, its choice being sometimes dictated by the solubility of the acid in the reaction mass. In the case of air oxidation at 120-200 °C, for the reaction mass to be maintained in the liquid state and for the loss of the product by entrainment to be reduced an elevated pressure is required (usually, from 0.2 up to 1-1.5 MPa). Part of the heat evolved is removed by the evaporation of the water formed and of the hydrocarbon (the hydrocarbon concentration in the gas phase must be outside the explosive limits).

The yield of aromatic acids is usually ≈ 90 percent, amounting sometimes to 95-97 percent. The by-products of a more complete oxidation of the methyl groups of alkylaromatic compounds are formic acid and carbon dioxide. Besides, by-products are also formed from the partial oxidation. The by-product of the incomplete

oxidation of *p*-xylene is *p*-carboxybenzaldehyde, which makes the polymer coloured.

Production of Dimethylterephthalate. It has turned out that in the above-mentioned four-step method of dimethylterephthalate production from *p*-xylene it is useful to carry out the steps of the oxidation of *p*-xylene and methyl-*p*-toluilate in a single reaction unit. Both esterification reactions (the esterification of *p*-toluic acid and monomethylterephthalate) are also effected in a single esterifying column. This makes it possible to increase the solubility of the acids

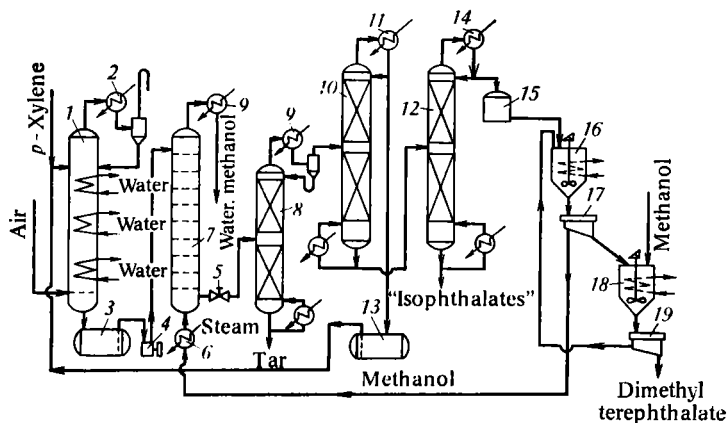


Fig. 6.18. Flow diagram of production of dimethylterephthalate:

1—oxidation column; 2—cooler; 3, 13, 15—collectors; 4—pumps; 5—reducing valve; 6—vaporizer-superheater; 7—esterifying column; 8—vaporizer; 9—condenser; 10, 12—fractionating columns; 11, 14—condenser-dephlegmators; 16, 18—autoclaves; 17, 19—centrifuges.

in the reaction mass and to reduce the number of steps and reaction units and to effect the separation of the products only after the esterification.

The flow diagram of the production of dimethylterephthalate is given in Fig. 6.18. The oxidation of a mixture of *p*-xylene and methyl-*p*-toluilate (in the ratio of 1 : 2) is effected in bubble column 1 fitted with cooling coils at 140-180°C and 0.6-1 MPa. The air preliminarily purified from impurities and compressed to the operating pressure is admitted into the lower part of the column through a distributing pipe. While bubbling through the reaction mass, the air entrains the xylene vapours, which are condensed in cooler 2, the condensate being returned to oxidation. The residual xylene is recovered from the off-gas by activated carbon (not shown in the flow diagram). In the batch process, the oxidation is completed at a residual *p*-xylene concentration of 1 percent in the reaction mass and with the degree of conversion of methyl-*p*-toluilate being equal to ≈50 percent. The oxygenated product contains 20-25 percent of *p*-

toluic acid, 30 percent of its methyl ester, 11-15 percent of terephthalic acid, 20-25 percent of its monoester and also small amounts of dimethylterephthalate and resinous impurities. Because of the presence in the starting *p*-xylene of its isomers and ethylbenzene, the oxygenated product is found to contain phthalic, isophthalic and benzoic acids and their esters.

The reaction mass is run to intermediate collector 3, from which it is continuously pumped by high-pressure pump 4 into the top of esterifying column 7 for esterification. The esterifying column is fitted with cap trays, and the liquid moves downwards through them. The vapours of methyl alcohol overheated in heater 6 move countercurrent to it. The esterification is effected at $\approx 250^\circ\text{C}$ and 2.5 MPa using the heat of the methanol vapours. The vapours of the alcohol, which is supplied in excess, carry off the water formed, contributing to the more successful completion of the equilibrium esterification process. The methanol and water vapours leaving esterifying column 7 are completely condensed in condenser 9; the methanol is recovered from this mixture in a special unit.

The esters leaving the bottom of esterifying column 7 are throttled and subjected to vacuum distillation at a residual pressure of 133 GPa. A mixture of esters is distilled off from the less volatile resinous impurities in vaporizer 8. The light distillate from fractionating column 10 is methyl-*p*-toluilate. It is condensed out in condenser-dephlegmator 11. Part of it is used to reflux the column, the remainder flowing into collector 13, from which it is sent to oxidation. The esters of dicarboxylic acids are passed from the still of column 10 to packed column 12 for vacuum fractionation, where the more volatile dimethylterephthalate distills out from the dimethyl esters of isomeric dicarboxylic acids ("isophthalates"). The ester is condensed in condenser-dephlegmator 14; part of this ester is returned to reflux the column, the remaining product running into collector 15. The still residue from column 12 still contains a considerable amount of dimethylterephthalate. It is transferred for crystallization from methanol solutions (not shown in the flow diagram). The "isophthalates" dissolve better in methanol, and the dimethylterephthalate is separated from them in the form of crystals and returned to fractionation.

For the final purification from the by-products and the production of high-purity dimethylterephthalate (99.9 percent) the crude product from collector 15 is subjected to two- or three-stage recrystallization from the methanol solutions: it is dissolved in methanol at 100°C in autoclaves 16 and 18, filtered off, washed and squeezed out on centrifuges 17 and 19. Here, the filtrate from the subsequent crystallization stage is used as the solvent for the preceding stage and the filtrate from the first stage is led to vaporizer-superheater 6 and then to the esterifying column. The overall yield of dimethylterephthalate with account taken of all the losses is 85-90 percent.

6.2.5.3. One-Step Oxidation of Methylbenzenes in Acetic Acid Solution

Because of the disadvantages of the above-described method of multistep oxidation of di- and polymethylaromatic compounds to di- and polycarboxylic acids, a one-step oxidation process has been explored. The investigations have culminated in the development of several variants of synthesis with the following common feature: they all employ acetic acid as the solvent.

In one group of methods, use is made of oxidation promoters (acetaldehyde, methyl ethyl ketone, paraldehyde) and of cobalt acetate as the catalyst. The promoters are oxidized together with the aromatic hydrocarbon, forming acetic acid. It is most likely that their

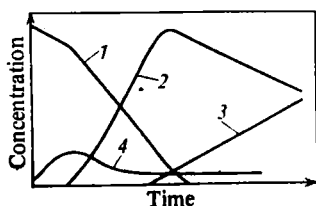
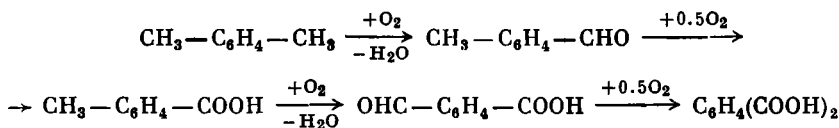


Fig. 6.19. The curves of accumulation of the products of oxidation of xylenes over a cobalt-bromide catalyst:

1—xylenes; 2—toluic acids; 3—phthalic acids; 4—aldehydes.

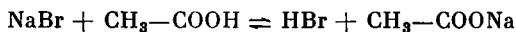
direct function is to maintain cobalt in the active trivalent state due to the oxidation of the divalent form by the transiently formed peracids. Another variant of the one-step process has found wider application, the one using a cobalt or cobalt-manganese catalyst promoted with bromine compounds, especially with NaBr.

The study of the oxidation of xylenes in the presence of metal bromide catalysts has shown that the process occurs in two distinct steps (Fig. 6.19, curves 2 and 3). First, only one methyl group is oxidized; only after the free xylene is used up does there begin the conversion of the monocarboxylic acid to the dicarboxylic acid; the second step occurs more slowly than the first. Curve 4 of aldehyde accumulation has a maximum soon after the reaction is started, following which the aldehyde concentration decreases and does not increase again at the second oxidation stage. Thus, the process occurs according to the following scheme:

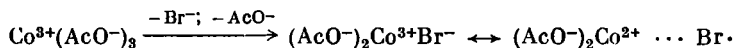


The mechanism of the action of metal-bromide catalysts is not yet fully clear. It is known that in the oxidation of the various compounds in their presence the reaction orders with respect to the reactants and the catalyst components differ strongly. It is presumed that the first bromide is hydrogen bromide, which is oxidized to ato-

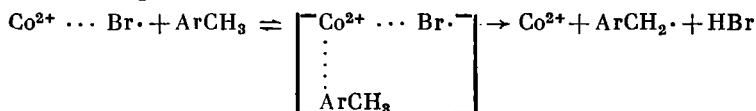
mic bromine; the atomic bromine participates in chain initiation:



Another viewpoint, which is probably more substantiated, is that the catalyst functions in the form of a mixed cobaltic salt, in which case the bromine assumes the properties of a radical:



The hydrocarbon becomes involved in the reaction due to the electron transfer through the bromide ion:



as a result of which the deactivating effect of the carboxyl groups does not manifest itself so strongly as in ordinary catalysis in the absence of bromide promoters.

The one-step method of xylene oxidation to dicarboxylic acids has been exploited industrially and it is even replacing the former multistep synthesis of terephthalic and isophthalic acids. According to the available data, the oxidation of the xylenes is carried out with air in a solution of acetic acid at 125–275 °C (better at 150 °C) and a pressure of 4 MPa. The reactor used is a bubble column or a stirred unit; the heat evolved is removed by the evaporation of the hydrocarbon, water and acetic acid. After the products are separated the acetic acid and catalyst are again led to oxidation, but the water formed retards the reaction, which is why it must be removed from the recirculating acetic acid.

Figure 6.20 presents the flow diagram of the one-step production of terephthalic acid by the oxidation of *p*-xylene. *p*-Xylene, air, recycle acetic acid and the catalyst are introduced into reactor 1 fitted with a stirrer (the losses of the acetic acid and catalyst are compensated for by feeding a fresh solution of the catalyst in acetic acid, which is not shown in the flow diagram). The reaction heat is removed by way of evaporation of acetic acid and water, whose vapours are condensed in cooler 2. The condensate is separated from the air in separator 3 and returned to the reactor.

The reaction mass is a suspension of terephthalic acid in a solvent. This suspension is filtered on centrifuge 4 (or on a filter), on which the terephthalic acid is washed with fresh acetic acid and sent for purification. The water is distilled off from the filtrate in fractionating column 5; the acetic acid with the catalyst dissolved in it is returned

from the still to the reactor 1. Because of much recycle, resinous impurities are accumulated in the acid, which is why part of the acid is led to column 6 for regeneration. The acetic acid is distilled off from the heavy residue and returned to the cycle. The residue is burned or the cobalt is regenerated from it.

The terephthalic acid produced by the one-step process needs special purification from *p*-carboxybenzaldehyde (in the two-step synthesis, purification is effected upon preparation and crystallization of the ester). To this end, use is made of a hydrogenation reaction in a water suspension at high temperatures and pressure; the impurities are transformed into more soluble compounds (hydroxy acids)

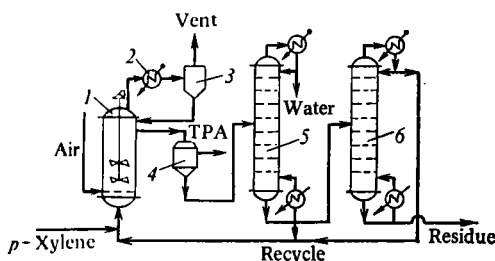


Fig. 6.20. Flow diagram of the one-stage synthesis of terephthalic acid: 1—reactor; 2—cooler; 3—separator; 4—centrifuge; 5—fractionating column; 6—acetic acid recovery column.

and dissolved in water. It has been suggested that the purification of terephthalic acid be effected by its esterification to dimethylterephthalate, which is then recrystallized. It has been reported that the direct synthesis of sufficiently pure terephthalic acid is possible; no special purification is required. The process can be accomplished by using a cobalt-manganese-bromide catalyst and optimum process parameters.

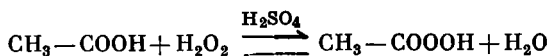
6.2.6. Oxidation of Saturated Aldehydes and Alcohols

In this section we shall consider the radical-chain reactions of oxidation at the functional groups already present in the molecule: the aldehyde groups (the production of peracids, carboxylic acids and anhydrides) and the hydroxyl groups in secondary alcohols (the production of ketones and hydrogen peroxide).

6.2.6.1. Oxidation of Aldehydes

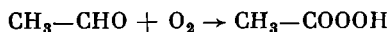
Synthesis of Peracids. This synthesis assumes an ever increasing importance in connection with the use of peracids for the manufacture of α -oxides (page 470); there is also a method of producing caprolactam with the aid of peracids (page 611).

Peracetic acid is the only peracid that has become industrially important because it is the cheapest of the peracids. The classical method of its production consists of the esterification of acetic acid by hydrogen peroxide in the presence of sulphuric acid as the catalyst:



The equilibrium relationships in this reaction are nearly the same as in the esterification of primary alcohols ($K \approx 4$). In order to increase the degree of conversion, an excess of acetic acid is used and, besides, part of water is distilled in vacuum.

Hydrogen peroxide is, however, an expensive compound; therefore, recourse is made to more economical methods of peracetic acid manufacture by the oxidation of acetaldehyde:



The by-product of this reaction is acetic acid.

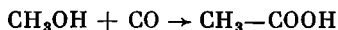
There are several methods for carrying out this process; they have been realized industrially or on a large pilot-plant scale. In one of these methods, the oxidation is effected using oxygen at 0 °C in a solution of acetone or ethyl acetate, the reaction being initiated by ozone. In another method, the oxidation is carried out with air in a solution of ethyl acetate at 30–40 °C and 2.5–4 MPa in the presence of cobalt acetate as the catalyst (0.0003 percent). The degree of conversion of acetaldehyde is 28 percent with the selectivity exceeding 90 percent. The reaction solution is subjected to fractionation. A gas-phase synthesis has also been carried out at 160–180 °C and with a deficiency of oxygen, which is admitted at several points along the length of the reactor. With the degree of conversion of acetaldehyde being equal to 15–20 percent the selectivity is 80 percent.

The experience in the exploitation of the plants for oxidation of acetaldehyde to peracetic acid has demonstrated the reliability of the safety measures used, which opens up the possibility of further development of economical methods of synthetic methods based on this reaction.

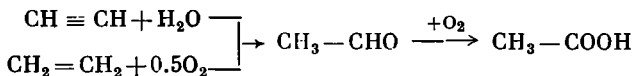
Synthesis of Acetic Acid. *Acetic acid*, $\text{CH}_3\text{—COOH}$ (b. p. 118°C, m.p. 16.6 °C), is miscible with water and most organic solvents. It is the most important of the aliphatic acids and is widely used in the food industry, as a solvent, an intermediate for the synthesis of monochloroacetic acids, solvents—the esters of acetic acid (ethyl acetate, butyl acetate, etc.), monomers (vinyl acetate) and other valuable compounds.

Acetic acid was formerly made by the dry distillation of wood and by the biochemical oxidation of ethyl alcohol. One synthetic method of oxidation of *n*-butane or light gasoline has already been described (page 409). The process for the synthesis of acetic acid from

methanol involves the carbonylation reaction:



This reaction may be based on coal. Of great practical value is the oxidation of acetaldehyde:



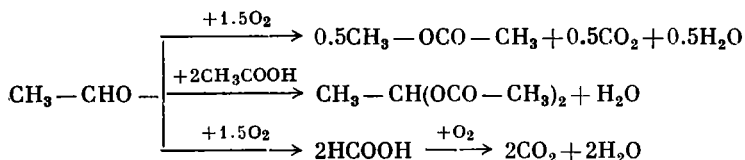
But in the general balance of acetic acid production one should take into account the quantity of acetic acid recovered from the production of cellulose acetate, where only one of the acetyl groups is used in the esterification by acetic anhydride:



The proportion of this regenerated acid may satisfy more than half the demand for it, especially with account taken of the combined synthesis of acetic acid and its anhydride from acetaldehyde described below.

In the liquid-phase oxidation of acetaldehyde to acetic acid, the catalyst most often used is manganese acetate (0.05-0.1 percent by weight based on acetaldehyde); the reaction is carried out at 50-80 °C. The choice of the catalyst, the quantity of the catalyst and the temperature is largely determined by the desire to attain a favourable ratio of the rates of the individual steps of the chain process. The use of other catalysts (cobalt, copper, and iron salts) and a decrease in temperature lead to an excessive accumulation of the peracid, which increases the explosion hazard of the production. The upper limit of the permissible maximum temperature is determined by the high volatility of acetaldehyde and by the intensive progress of side reactions, which lower the yield of acetic acid.

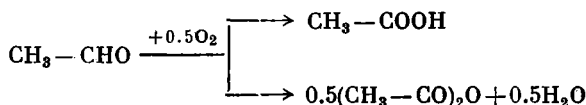
The by-products in the oxidation of acetaldehyde are methyl acetate, ethylidene diacetate, formic acid and carbon dioxide:



Because of the high volatility of acetaldehyde (b.p. 21 °C) its oxidation is effected in a solution of acetic acid using ordinary or oxygen-enriched air or technical oxygen at 65-70 °C and 0.4-0.5 MPa. The reactor is a bubble column fitted with cooling coils (see Fig. 6.5b, page 396); the oxidizing gas is introduced at several points along the height of the column. The crude acid is withdrawn through the side overflow pipe and is subjected to fractionation: the volatile com-

pounds are distilled out first (methyl acetate, unconverted acetaldehyde) followed by acetic acid; the heavy residue (ethylidene diacetate, resins) is left in the still. In order to obtain the high-quality acid, the impurities are oxidized by permanganate, this being followed by the final fractionation.

Joint Synthesis of Acetic Acid and Acetic Anhydride. It has been said earlier that under certain conditions the oxidation of acetaldehyde to the carboxylic acid is accompanied by the formation of acetic anhydride:



Since the formation of the anhydride inevitably involves the liberation of water, which can hydrolyze it to the acid, one of the conditions for the simultaneous synthesis of the anhydride and acid is the rapid removal of water. This was formerly achieved by using azeotropic mixtures (ethyl acetate, diisopropyl ether), but later it was found that they could be dispensed with. The most important factors that control the relative yield of the acid and anhydride have proved to be:

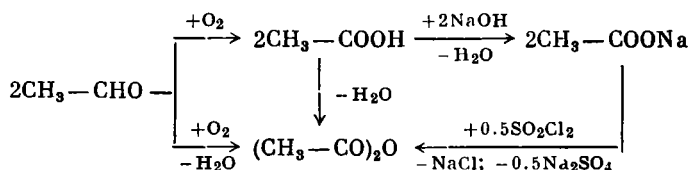
(1) the composition of the homogeneous catalyst, namely a mixture of cobalt or manganese salts with copper salts ($\text{Co} + \text{Cu}$, $\text{Mn} + \text{Cu}$) in an approximate ratio of 1 : (1-3) and also its high concentration in the reaction solution;

(2) the use of a dilute oxidizing gas (7-9 percent by volume of O_2) and the occurrence of the process in the diffusional or near-diffusional region (which contributes to a decrease in the oxygen concentration in the liquid and to an increase in the concentration of the radicals $\text{CH}_3-\dot{\text{C}}=\text{O}$, which are intermediates on the route to the anhydride).

Under the conditions described the ratio of the acid and anhydride formed can be increased up to (3-5) : (7-5).

The production of acetic anhydride from the salts of acetic acid and the acid chlorides of inorganic acids and also by the dehydration of acetic acid and via a ketene has been described earlier (page 212).

The direct oxidation of acetaldehyde to a mixture of the anhydride and acetic acid is the most economical and it replaces all other methods:



Two methods are employed for the joint synthesis of these compounds. In the first, the process is carried out in a bubble column in the medium of ethyl acetate at 50-70 °C and ≈ 0.4 MPa. The oxidation is effected using air (not oxygen) in the presence of mixed catalysts (for example, copper and cobalt acetates in a ratio of 10 : 1 or 2 : 1). The solvent, acetaldehyde and catalyst solution are continuously fed into the oxidation column and air is bubbled through the reaction mixture. The vapours entrained by the air are condensed in a reflux cooler; the water is separated and the ethyl acetate is returned to the column. Volatile acetaldehyde is absorbed from the gas by water and is then regenerated by distillation. The reaction mass is withdrawn from the oxidation column and sent for separation; the mixture of the solvent, water and unconverted acetaldehyde is distilled off first. Then, in the other columns the acetic acid, acetic anhydride and catalyst solution are distilled off successively, the catalyst solution being then returned to the oxidation step.

In the second method, the oxidation is carried out at 55-60 °C in the absence of a foreign solvent with the aid of the same catalysts (say, copper and cobalt acetates in a ratio of 3 : 1) using air depleted in oxygen (7-9 percent by volume of O_2). A mixture of fresh air and recycle gas containing acetaldehyde vapours is fed into the reactor, which is a column fitted with cooling coils. The reaction mass consists mainly of acetic acid and acetic anhydride with the catalyst dissolved in them. A distinctive feature of the method is that a large amount of the gas is introduced into the reactor through a special gas-distributing arrangement, this contributing to a vigorous agitation of the liquid. The products are withdrawn (in the form of vapours) together with the effluent gas, and the catalyst solution is left in the reactor and can be used for a long period of time until it is deactivated.

The flow diagram of the joint synthesis of acetic acid and acetic anhydride is shown in Fig. 6.21. Fresh purified air supplied by air blower 1 at a pressure, which is slightly above atmospheric, is mixed with the recycle gas containing the vapours of acetaldehyde. The resulting mixture [7-9 percent (by volume) of oxygen, 25-30 percent (by volume) of acetaldehyde, 1 percent (by volume) of acetic acid, the remainder being nitrogen] is introduced below the distributing grid of reactor 2 and bubbles through the catalyst solution, entraining the product vapours. The steam-gas mixture is partially cooled with water in cooler 3 and the resultant condensate is returned to the reactor in order to maintain a constant level of the liquid in it. This is followed by additional cooling in cooler 4 and saturation tower 5, into which acetaldehyde is introduced and the residual products are condensed from the gas by the evaporation of the acetaldehyde.

The steam-gas mixture from the top of the saturation tower 5

is drawn off by circulation gas blower 6 and returned to be mixed with fresh air and then to the reactor. But part of the circulating gas has to be withdrawn from the system in order to avoid excessive dilution. This off-gas, which contains a large amount of acetaldehyde, is washed in scrubber 7 by a small amount of acetic acid (to absorb the vapours of acetic anhydride) and then in absorber 8 with water, which entrains all of the acetaldehyde. The acetaldehyde

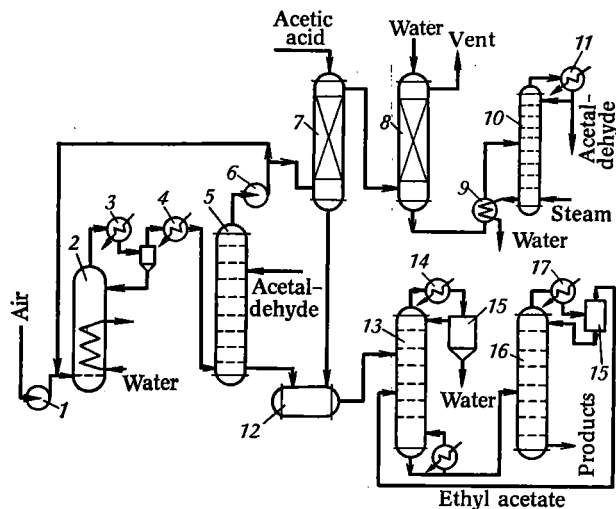


Fig. 6.21. Flow diagram of the combined synthesis of acetic acid and acetic anhydride:

1—air-blower; 2—reactor; 3, 4—coolers; 5—saturator; 6—gas blower; 7—scrubber; 8—absorber; 9—heat exchanger; 10, 16—fractionating columns; 11, 14, 17—dephlegmators; 12—collector; 13—azeotropic drying column; 15—separator.

is recovered from the resultant mixture in fractionation column 10 equipped with brine dephlegmator 11 and returned to saturator 5 and then to the reaction. The spent air leaving absorber 8 is discharged into the atmosphere.

The condensate leaving saturator 5 and scrubber 7 runs into collector 12. This crude product contains 58-60 percent (by weight) of acetic anhydride, 28-30 percent (by weight) of acetic acid, 9-10 percent (by weight) of water, 1-1.2 percent (by weight) of ethylidene diacetate, a small amount of acetaldehyde and formaldehyde. Because of the possibility of the hydrolysis of the anhydride (especially at elevated temperature), the azeotropic distillation of water with ethyl acetate is effected in column 13 equipped with dephlegmator 14 and separator 15. This is followed by the distillation of ethyl acetate from the product mixture in column 16; the ethyl acetate is then returned to azeotropic purification. Acetic acid and acetic an-

hydride are produced in pure form after additional fractionation (not shown in the flow diagram). The yield of the products is 95 percent of the theoretical.

6.2.6.2. Oxidation of Secondary Alcohols. Production of Hydrogen Peroxide

The catalytic oxidation of secondary alcohols gives ketones, which are then oxidized further with the degradation of the chain and formation of carboxylic acids. A different result is obtained in the oxidation of secondary alcohols without the aid of catalysts: at 90-140 °C they are converted into a ketone and hydrogen peroxide:

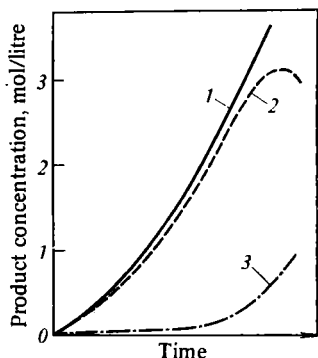
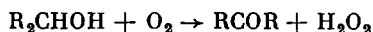


Fig. 6.22. The curves of the yield of products in the oxidation of isopropyl alcohol:

1—acetone; 2—hydrogen peroxide; 3—carboxylic acids.

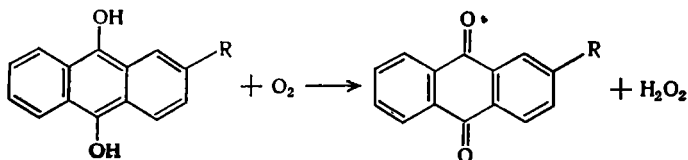
As the reaction products are gradually accumulated degradation processes are developed, which lead to the formation of carboxylic acids. These acids exert a catalytic effect on the decomposition of hydrogen peroxide, as a result of which the curve of its accumulation in the reaction mixture passes through a maximum (Fig. 6.22). The

process therefore is carried out to a low degree of conversion and a dilute solution of the products in the alcohol is obtained, the alcohol being then returned to oxidation.

This method is employed on an industrial scale for the oxidation of isopropyl alcohol to produce acetone and hydrogen peroxide. The process is effected in a bubble column at 90-140 °C and 1.4-2.1 MPa. The initiator is hydrogen peroxide itself, which (when the plant is started or the process is operated batchwise) is added to the alcohol in a concentration of 0.5-1 percent. The resultant mixture is diluted with water and an inhibitor of peroxide decomposition is added to it; the mixture is then distilled to isolate acetone, unconverted alcohol and aqueous hydrogen peroxide. This process is regarded as the main source of hydrogen peroxide; it has the advantage of the simultaneous formation of a valuable coproduct—acetone.

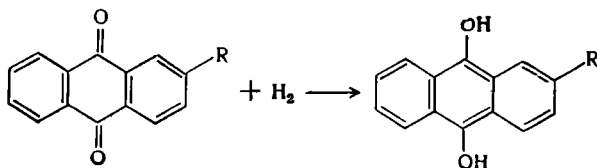
Another method of production of hydrogen peroxide, which is analogous to the above-described process, consists of the oxidation of 2-alkylanthrahydroquinone in a solution of an aromatic hydro-

carbon (a xylene) and 2-octanol (the choice of 2-alkylanthrahydroquinone and a mixed solvent is dictated by the requirement² of better solubility);



The oxidation is carried out with air in a hollow, packed or sectioned column at 40-80 °C and a pressure of up to 0.7 MPa.

The resulting hydrogen peroxide is extracted by water and the solution of 2-alkylanthraquinone is sent for hydrogenation in the presence of a nickel catalyst:



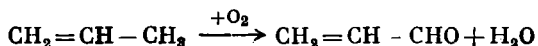
The hydrogenation reaction is effected until about 50 percent conversion of the quinone is attained, which corresponds to the formation of more soluble quinhydrone, following which the solution is again sent to oxidation. This effects the oxidation-reduction cycle, which leads to the formation of hydrogen peroxide from molecular oxygen and hydrogen. As compared with the electrochemical synthesis of hydrogen peroxide, organic methods of its production consume much less electric power.

Hydrogen peroxide is widely used in medicine, as a bleaching agent, an intermediate in organic synthesis (the production of organic peroxides, epoxides, glycols, peracids) and also as a rocket fuel oxidizer.

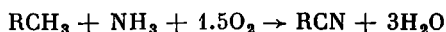
6.3. Heterogeneous-Catalytic Oxidation of Hydrocarbons and Their Derivatives

The heterogeneous-catalytic oxidation process has become very important for the realization of a number of processes that cannot be successfully accomplished by means of radical-chain oxidation reactions. The most important processes are:

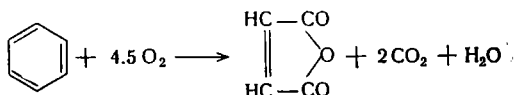
(1) the oxidation of olefins and their derivatives across the saturated carbon atom with the double bond remaining intact:



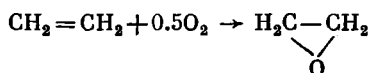
(2) the oxidative ammonolysis of olefins and other hydrocarbons with the formation of nitriles:



(3) the oxidation of aromatic and other hydrocarbons with the formation of the inner anhydrides of di- or tetracarboxylic acids:



(4) the direct synthesis of ethylene oxide:



All these processes are of great practical value because the products obtained are widely used as monomers (acrylic and methacrylic acids, acrylonitrile, maleic and phthalic anhydrides) and as intermediates for the synthesis of plasticizers, solvents, other monomers, etc. (phthalic anhydride, ethylene oxide, nitriles, acrolein).

6.3.1. Scientific and Engineering Foundations of the Process

6.3.1.1. Heterogeneous Oxidation Catalysts and Reaction Mechanism

Of the catalysts used for the heterogeneous oxidation of organic compounds, the following have assumed practical importance:

1. Metals—Cu and Ag, of which the easily oxidizable copper presumably functions in the form of oxides formed in the surface layer. Other metals (Pt, Pd) lead to the complete oxidation to CO_2 and H_2O .

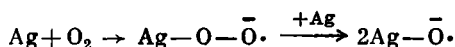
2. The oxides of transition metals— $CuO + Cu_2O$, V_2O_5 ; other oxides are either inactive or lead to complete oxidation.

3. Mixtures of transition-metal oxides and salts, especially zinc, cobalt and bismuth vanadates, stannates, tungstates and molybdates ($ZnO \cdot V_2O_5$, $CoO \cdot WO_3$, $Bi_2O_3 \cdot MoO_3$), which may contain the corresponding oxides and their compounds in the form of separate phases. In contrast, ferrites and chromites cause complete oxidation.

The catalysts listed above are used in the form of turnings or gauzes (Cu), grains of the catalyst itself (V_2O_5) or supported on porous carriers (Ag, CuO, salts), to which promoters are sometimes added.

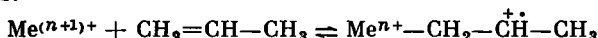
An important role in the mechanism of heterogeneous oxidation reactions is played by the adsorption of reactants on the catalyst sur-

face. Oxygen is sorbed on metals very rapidly with subsequent slower penetration into the near-surface layer. As a result, base metals form oxides, and for silver the process boils down to chemisorption leading to a considerable change of the properties of the near-surface layer. It is believed that oxygen is sorbed on the catalyst without being dissociated or with dissociation of the molecule, the metal supplying the required electrons and converting the adsorbed oxygen into the state of a radical-ion:



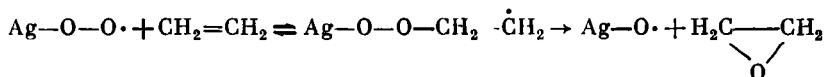
A similar type of oxygen chemisorption occurs on the oxide and salt catalysts, where sorption takes place on a transition-metal ion. The ion is oxidized to the higher valent state.

Hydrocarbons are sorbed on metals relatively weakly and reversibly. They are sorbed more strongly on oxide and salt catalysts, the electrons required for the formation of a bond being donated by the olefin molecule, which is transformed to the state of a chemisorbed ion-radical:

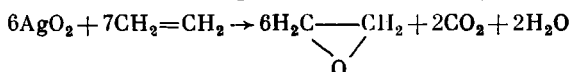


The metal ion is here reduced to one of the lower valent forms. As a result of the combined action of oxygen and the hydrocarbon, the metal ions are found to be in different valent states, which corresponds on the average to some fractional value. For example, upon oxidation of naphthalene with air the vanadium ion has an average valency of ≈ 4.3 instead of 5 in V_2O_5 . Obviously, the state of the metal ion is determined by the redox properties of the medium and depends on the oxygen-hydrocarbon ratio, on the presence of water vapours, etc. Here, at the start of the operation the catalyst gradually assumes a state which is stable under given synthesis conditions: variation of the conditions may result in a change of its activity and selectivity.

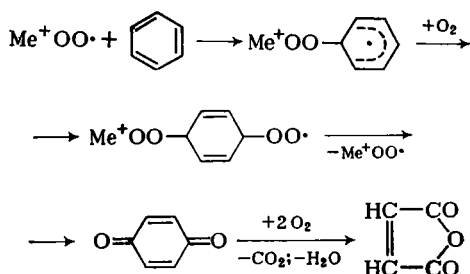
There are two principal types of the mechanism of heterogeneous-catalytic oxidation. In one, the hydrocarbon is sorbed on the oxidized surface of the catalyst; first it is sorbed at the oxygen ion-radical and then reacts with it with the formation of oxidation products. A typical example is the synthesis of ethylene oxide:



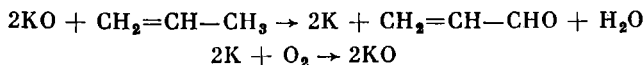
It is presumed that the products of complete oxidation are obtained from ethylene and $\text{Ag}-\text{O} \cdot$; this corresponds well to the possible maximum selectivity of this process (85 percent):



An example of the same mechanism is the oxidation of benzene to maleic anhydride, which proceeds via the intermediate formation of quinone:



Another frequently used mechanism of heterogeneous-catalytic oxidation is called the oxidation-reduction (redox) mechanism. The hydrocarbon sorbed on the metal ion is oxidized by the oxygen of the catalyst lattice; the metal is reduced to the lowest valent state and then reacts with the oxygen again and changes to the initial form:



This mechanism is characteristic of the oxidation of olefins and methylbenzenes. It is verified by the fact that the expected products can be obtained on the catalyst in the absence of oxygen, and the steps of hydrocarbon and catalyst oxidation can be carried out separately.

The two mechanisms outlined above are the extreme cases; there are also intermediate mechanisms. These intermediate mechanisms have not yet been fully clarified, because the structure of the surface products and their role in the oxidation are not yet clear.

6.3.1.2. Kinetics and Selectivity of Heterogeneous-Catalytic Oxidation

Not infrequently the study of the kinetics of the heterogeneous-catalytic oxidation of olefins and other organic compounds give differing results. One may, however, come to the general conclusion that in the kinetic region the oxidation reaction obeys the Langmuir-Hinshelwood equation:

$$r = k \frac{P_{\text{RH}} P_{\text{O}_2}}{1 + \sum b_i P_i}$$

This model is often approximated by power functions. For instance, the following equation has been derived for the oxidation of ethylene to ethylene oxide:

$$r = k P_{\text{C}_2\text{H}_4}^{n_1} P_{\text{O}_2}^{n_2}$$

where the apparent orders with respect to the reactants are (according to data obtained by different authors): $n_1 = 0.45$, $n_2 = 0.55-1$. This difference is due largely to the reaction conditions with an excess of the olefin or with an excess of oxygen (i.e., outside the lower or the upper explosive limit of the mixtures). In the first case, the oxidation rate depends on the oxygen partial pressure, being of near-zero order with respect to the olefin, as, for example, in the oxidation of propylene to acrolein with an oxygen deficiency:

$$r = k \frac{P_{\text{O}_2}}{1 + b P_{\text{prod}}}$$

Ethylene is oxidized in an excess of oxygen; the reaction rate is independent of the oxygen concentration in this region, being of near-first order with respect to the olefin:

$$r = k \frac{P_{\text{C}_2\text{H}_4}}{b_1 P_{\alpha\text{-oxide}} + b_2 P_{\text{CO}_2}}$$

From the last equation it can be seen that the reaction may also be retarded by the by-products of complete oxidation.

With an excess of oxygen the oxidation of propylene to acrolein obeys the following kinetic equation:

$$r = k \frac{P_{\text{C}_3\text{H}_6}}{1 + b P_{\text{prod}}}$$

The same equation holds for the oxidative ammonolysis of propylene, the rate of which under certain conditions is independent of the partial pressures of oxygen and ammonia. The last two kinetic equations are close to the redox mechanism, in which the oxidation of the reduced active centres of the catalyst proceeds rapidly and does not limit the overall velocity of the process. In this case the oxidation and oxidative ammonolysis are found to be first-order with respect to propylene ($r = k P_{\text{C}_3\text{H}_6}$).

Finally, the oxidation of benzene to maleic anhydride and the oxidation of naphthalene to phthalic anhydride are first-order in oxygen and from zero to first order in the aromatic hydrocarbon (depending on the reactant ratio). These reactions are also retarded by the anhydrides formed:

$$r = k \frac{P_{\text{O}_2} P_{\text{ArH}}^{0.5}}{1 + b P_{\text{anh}}}$$

on the ordinate characterizes the contribution of the parallel route and the descending character of the curve points to the consecutive conversion to the products of complete combustion. Evidently, with account taken of the cost of the recovery of unreacted hydrocarbon, for each process there exists a certain optimum degree of conversion determined by economic factors. With other conditions being equal, it is controlled in two ways: by varying the contact time or by the use of an oxygen deficiency.

Finally, the most important role is played by the catalyst itself, the method of its preparation, etc. The activity and selectivity of the catalyst can be strongly changed by addition of various modifiers or by using mixtures of oxides and salts. For example, some catalytic poisons (the halogens, selenium), while deactivating the silver catalyst used for the oxidation of ethylene, increase its selectivity substantially. Molybdenum and bismuth oxides used separately cause the complete combustion of olefins, but when they are in the form of bismuth molybdate ($\text{Bi}_2\text{O}_3 : \text{MoO}_3 = 1 : 2$) they are selective catalysts for the heterogeneous oxidation of propylene. The catalyst support, the grain size of the catalyst, its porosity, etc., play a significant part. Because of the possibility of a consecutive oxidation of the end product and of the high rate of the chemical reaction itself on the catalyst surface the occurrence of the process in the intradiffusion region is highly undesirable, which is why use is made of catalysts with small grains and relatively large pores.

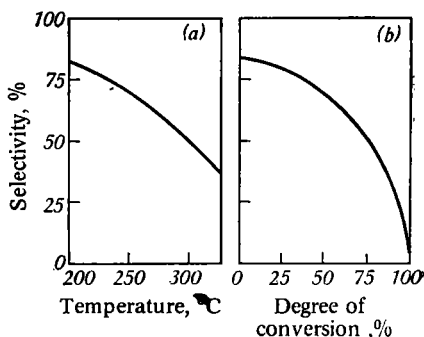


Fig. 6.23. Dependence of the selectivity of the oxidation of ethylene on temperature (a) and the degree of conversion (b).

6.3.1.3. Reactors for Heterogeneous-Catalytic Oxidation

These reactions are often carried out at atmospheric pressure, but an ever increasing number of plants appear, where heterogeneous-catalytic oxidation is carried out at a pressure ranging from 0.3 to 2 MPa, which allows one to intensify the process, to reduce the size of the vessels and to simplify the separation of unreacted hydrocarbon and reaction products. Depending on the process, the temperature varies from 250-300 up to 400-500 °C. Since mixtures of hydrocarbons with oxygen present explosion hazards, there are several means for staying outside the explosive limits: oxidation by recycle gases with addition of fresh air or oxygen at a low olefin

concentration (3-5 percent by volume); oxidation of excess hydrocarbon by a small amount of technical oxygen; dilution of the mixture with steam.

One of the key problems in the design of reaction vessels for gas-phase oxidation is the removal of heat and prevention of local overheating. Because of the low coefficients of heat transfer from the gas to the wall, this problem is more complicated than in the case of liquid-phase oxidation processes. An ever increasing role is played

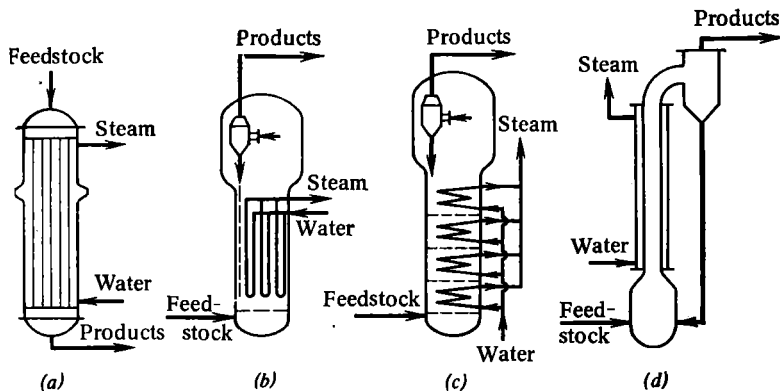


Fig. 6.24. Reactors for heterogeneous-catalytic oxidation:

a—tubular fixed-bed reactor; b—fluidized-bed reactor; c—reactor with a sectioned fluidized bed; d—reactor with an ascending catalyst flow.

by the problem of the increase of the thermal efficiency of reaction units, which boils down to the utilization of the reaction heat for the generation of steam.

Since oxidation reactions are strongly exothermic, adiabatic reactors have not found application for this process. Wide use is made of tubular reactors with a fixed catalyst bed placed in the tubes and cooled through the intertube space by a coolant (Fig. 6.24a). The tubes are 10-25 mm in diameter, which favours the removal of heat and the establishing of a more uniform temperature along the diameter. In order to use the bulk of the catalyst more effectively, preheated reagents are introduced into the reactors. The best means for removing the heat evolved is the vaporization in the intertube space of the water condensate, which generates steam of the pressure depending on the reaction temperature. Sometimes, use is made of a special heat-transfer agent for cooling (molten salts, Dowtherm), which in turn is cooled by the boiling water condensate that generates process steam. The advantages of tubular contact reactors are the simplicity of their design and operation and also their closeness to the plug-flow model, this favouring the increase of the selectivity; the shortcomings of such reaction vessels are the nonuniformity of

the temperature along the catalyst bed, the small useful volume and, as a consequence, the large quantity of metal consumed.

Many oxidation processes are carried out in reactors with a fluidized bed of a heterogeneous catalyst (Fig. 6.24b). They are similar to those considered earlier for catalytic cracking, the only difference being the absence of regeneration units, since upon oxidation the formation of gum and carbon black is insignificant and the catalyst retains its activity for many months and even for several years. The reactants may be introduced cold and the catalyst is used in a hard microspherical form and is in a state of constant whirling.

As usual, the reactor is fitted with a distribution grid, cooling pipes, in which steam is generated, and with cyclones for trapping the particles entrained by the gas. Such a reactor provides an ideal solution to the problem of heat removal and maintenance of uniform temperature, but back-mixing occurs which lowers the process selectivity.

In order to eliminate the last-named shortcoming, use is made of sectioned reaction vessels with a fluidized catalyst bed, in which there are several grids (in addition to the distribution grid) which divide the reaction volume into sections (Fig. 6.24c). A decrease in back-mixing can also be attained in reactors with an ascending catalyst flow (Fig. 6.24d), which moves upwards together with the gas. The reaction tube is cooled by a jacket with the boiling water condensate.

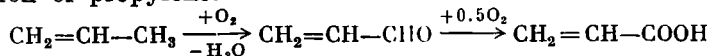
The catalyst is separated in the separator or cyclone and returned through the pipe into the lower part of the reactor called the proportioning section. In the reactor shown in Fig. 6.24d the heat-transfer conditions are worse than in the preceding reactors since external cooling is less effective with a rather wide reaction tube. However, such a reactor can also be constructed as a multitubular unit cooled through the intertubular space.

In choosing the material of the apparatus for gas-phase oxidation one has to take into account the fact that not only carboxylic acids but also mixtures of carbon dioxide and steam, which are always formed during the reaction, can cause corrosion. Moreover, some metals and their oxides can catalyze undesirable reactions of complete oxidation. This is why all the reactors considered above are usually constructed of alloy steels.

6.3.2. Oxidation of Olefins at the Saturated Carbon Atom

6.3.2.1. Production of Acrolein and Acrylic Acid

These compounds are produced by the heterogeneous-catalytic oxidation of propylene:



Acrolein, $\text{CH}_2=\text{CH}-\text{CHO}$ (b.p. 52.5°C) is a liquid with a disagreeable choking odour. It dissolves well in water and forms an azeotropic mixture with it. Upon prolonged storage or on heating it is readily polymerized into cyclic or linear polymers, which is why inhibitors have to be used for its processing. Acrolein is extensively used for the production of acrylic acid and its esters, allyl alcohol, synthetic glycerine and other products, including methionine, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, which is a valuable feed supplement for birds.

Acrylic acid and its esters have already been described (page 240). They were once produced from acetaldehyde and HCN and later from acrylonitrile, but because of the use of the expensive raw material, sulphuric acid, and the formation of ammonium sulphate, these methods are replaced by the direct oxidation of propylene.

Oxidation of Propylene to Acrolein. The process is accompanied by the formation of by-products: acetaldehyde, acetone, acetic and acrylic acids, CO and CO_2 . Just as in any heterogeneous oxidation reaction, carbon monoxide and carbon dioxide are formed not only from acrolein but also concurrently from propylene.

The process can be made selective by using catalysts that direct the oxidation to the side of the predominant formation of acrolein. The first catalysts used were supported cuprous oxide (0.1-1.5 percent of Cu_2O on pumice, carborundum or Al_2O_3) or even the copper tubes of the reactor. Later there were developed catalysts from bismuth molybdate ($\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$) and from bismuth phosphomolybdate ($\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3 \cdot \text{P}_2\text{O}_5$), containing promoters (tellurium and copper oxides). These catalysts make it possible to attain high selectivity with a short contact time and a moderate temperature. For example, the contact time recommended for cuprous oxide is 0.2 s at $370-400^\circ\text{C}$ or about 2 s at $320-350^\circ\text{C}$. When molybdate catalysts are used, a higher temperature is permissible ($400-500^\circ\text{C}$) with a contact time of 1-2 s. These parameters depend to a certain extent on the pressure, which varies from 0.1 to 1 MPa, depending on the reaction vessel used.

The composition of the feedstock is determined by the explosive concentration limits, which is why steam (25-50 percent by volume) is always added to the mixture introduced into the reactor; steam also contributes to the increase of the selectivity due to the desorption of acrolein. The oxidizing gas used is technical oxygen or air. Air is cheaper than technical oxygen, but it dilutes the reaction gases and complicates the recovery and recirculation of the compounds. The ratio of propylene to oxygen (or air) in the feedstock may differ: there are reaction units operating with an excess of propylene (42-44 percent by volume of C_3H_6 , 8-10 percent by volume of O_2 , and 46-50 percent by volume of H_2O) or, on the contrary, with an excess of oxygen or air (7-8 percent C_3H_6 , 67 percent of air, 25 per-

cent of H_2O). Obviously, in the first case the unconverted propylene must be recycled, which is why oxygen is used rather than air. The degree of conversion with respect to the reagent, which is deficient, varies from 60 to 100 percent and the selectivity ranges from 70 to 90 percent.

The reaction is carried out in various reactors, but shell-and-tube reactors with a fixed catalyst bed and cooled by molten salts have found widest application. The melt circulates through a waste-heat boiler, producing high-pressure steam. The reaction gases then pass through the absorber, where the oxidation products are absorbed by water and a 1.5-2 percent solution of acrolein is obtained, which contains acetaldehyde, acetone and a small amount of propionaldehyde. The acetaldehyde is easily separated by fractional distillation, and the acrolein is purified from the close-boiling propionaldehyde (b.p. -49°C) by extractive distillation with water. The resultant acrolein contains 99 percent of the major component with an impurity of water and propionaldehyde.

Production of Acrylic Acid. The oxidation of acrolein to acrylic acid is also effected by using oxide bismuth-molybdenum catalysts with various promoters (Te, Co, P, etc.), but the reaction conditions are milder: the temperature is $200\text{--}300^\circ\text{C}$ and the contact time 0.5-2 s. The by-products formed are acetic acid and oxides of carbon with the selectivity of the process exceeding 90 percent.

It was economical to combine the oxidation of propylene to acrolein with the oxidation of acrolein to acrylic acid on an industrial scale. Originally, the one-step process of direct oxidation of propylene to acrylic acid was carried out in a single reactor, which reduced the capital investment. The yield of acrylic acid was not high (<70 percent) because the combination of the two steps with different optimum conditions could not favour the increase of selectivity.

At present, the two-step process has achieved a dominant position (Fig. 6.25). A mixture of 4-7 percent (by volume) of propylene, 50-70 percent of air and 25-40 percent of steam is introduced into first-stage reactor 1. The principal reaction taking place in this reactor is the oxidation of propylene to acrolein at $300\text{--}400^\circ\text{C}$. Without being separated the reaction gases enter second-stage reactor 3, where a temperature of $250\text{--}300^\circ\text{C}$ is maintained and the oxidation of acrolein to acrylic acid takes place. The two reactors are tubular units containing a fixed catalyst bed and cooled by molten salts, which give off their heat in heat-utilization units 2, thereby producing steam. The reaction gases leaving reactor 3 are treated with water in absorber 4, where the acrylic acid is absorbed; the gas is then discharged into the atmosphere.

The resulting aqueous solution contains 20-30 percent by weight of acrylic acid with an impurity of acetic acid. The major product is isolated by extraction (not shown in the flow diagram) by a suf-

ficiently low-boiling organic solvent. It is distilled out of the extract and recycled to the extraction unit, the acrylic and acetic acids being separated by the fractionation of the residue. The yield of acrylic acid is said to be 80-85 percent based on propylene.

Oxidation of Isobutylene to Methacrolein and Methacrylic Acid. Methacrolein itself has limited application, which is why the process

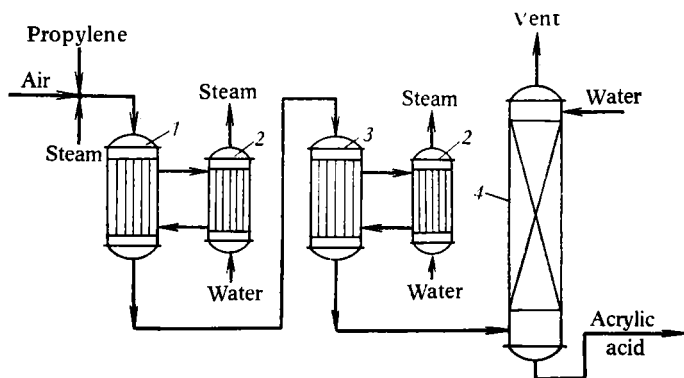
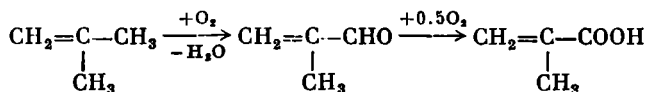
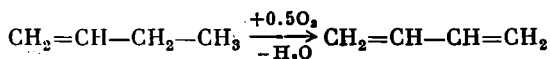


Fig. 6.25. Flow diagram of the two-stage oxidation of propylene to acrylic acid: 1—first-stage reactor; 2—waste-heat boiler; 3—second-stage reactor; 4—absorber.

is of practical value due mainly to the synthesis of methacrylic acid. It also proceeds in two steps:



The first step is analogous to the production of acrolein and is accompanied by the formation of the same by-products, but the selectivity of the reaction is lower. Multicomponent catalysts have been proposed for this process; they are based on molybdenum with the oxides of Bi, Co, Ni, Te, V, Sb, Fe, P, etc., being added. The oxidation is carried out at 350-450 °C and atmospheric pressure; the mixture of isobutylene and air is diluted with steam. The 90-98 percent conversion of isobutylene with a selectivity of 70-90 percent has been reported. Even better results are obtained by the oxidation of a mixture of isobutylene and *n*-butylene; the former is oxidized to methacrolein and the latter undergoes oxidative dehydrogenation to butadiene:



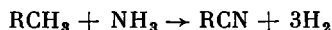
At 390 °C and with a contact time of 4 s the degree of conversion of olefins is 96-98 percent with the selectivity being equal to 80-90 percent for methacrolein and up to 90 percent for butadiene.

The second step—the oxidation of methacrolein to methacrylic acid—encounters serious difficulties as compared with the oxidation of acrolein. In both cases, no radical-chain processes are applicable because of the polymerization of unsaturated aldehydes. Attempts have been made to use catalysis with copper or silver for the liquid-phase process, the oxidation by peracids and other methods, but major attention has been devoted to the development of sufficiently selective heterogeneous catalysts for the gas-phase oxidation. One of these catalysts is the oxide phosphomolybdate catalyst to which are added the oxides of Te and Sb, the NH_4^+ ions and the ions of alkali and alkaline-earth metals. At 250-350 °C and atmospheric pressure and with the degree of conversion of methacrolein being 80-90 percent the selectivity for methacrylic acid can be increased up to 70-80 percent.

The above-described method of production of methacrylic acid is now being developed to the commercial stage. It is very promising both from the economic and technical standpoint and is expected to replace the other methods of manufacturing methacrylic acid and its esters.

6.3.3. Oxidative Ammonolysis of Hydrocarbons

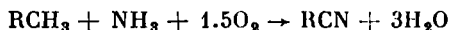
Hydrocarbons are capable of reacting with ammonia at a high temperature to form nitriles:



Nitriles are also obtained from aldehyde and ammonia via the intermediate step of dehydrogenation of imines:



It was intriguing to combine such processes with oxidation and, as a result, there was developed the *oxidative ammonolysis* (or *ammonoxidation*) of hydrocarbons:

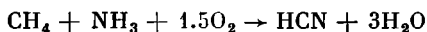


The reaction was first developed by Andrussov in the thirties on methane; in the fifties and sixties it was extended to olefins and methylbenzenes.

6.3.3.1. Synthesis of Hydrogen Cyanide

Hydrogen cyanide (hydrocyanic acid), $\text{HC}\equiv\text{N}$, is a liquid (b.p. 25.7 °C) noted for very high toxicity. Hydrogen cyanide and its salts are used on a rather large scale for the production of some nitriles.

les, cyanogen chloride and cyanuric chloride (page 151), acetone cyanohydrin and methacrylates (page 240) and also in electroplating and for the extraction of precious metals from ores. The present-day method of production of hydrogen cyanide involves the oxidative ammonolysis of methane:

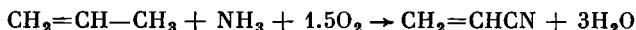


The reaction occurs almost instantly at 1000 °C over a platinum-rhodium or platinum-iridium catalyst used in the form of several layers of a gauze made of thin wires of the corresponding alloy. The starting mixture of methane, ammonia and oxygen (in the form of air) is fed in the ratio of 1.1 : 1.0 : 1.5. The by-products formed are CO and CO₂ (due to the oxidation of methane), H₂ and N₂ (due to the decomposition of ammonia into its elements), but the selectivity for HCN is fairly high, being equal to 80-83 percent.

It is believed that the mechanism of this reaction involves the intermediate formation of the chemisorbed radicals $\cdot\text{NH}_2$, $\cdot\text{NH}$, $\cdot\text{NHOH}$, $\cdot\text{NOH}$, etc., which make relatively unreactive methane enter into the reaction. The intermediate formation of methylamine, CH_3NH_2 , and methyleneimine, $\text{CH}_2=\text{NH}$, is also possible.

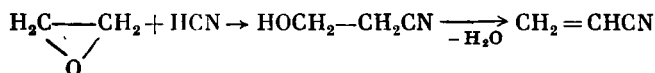
6.3.3.2. Oxidative Ammonolysis of Olefins and Methylbenzenes

These reactions differ significantly from the synthesis of hydrocyanic acid in mechanism, catalysts and reaction conditions. Their industrial significance is due to the production of acrylonitrile from propylene:



Acrylonitrile is a liquid (b.p. 77.3 °C), which is only sparingly soluble in water (7.3 percent at 20 °C) and forms an azeotropic mixture with it, which contains 12.5 percent of water and boils at 70.7 °C. Acrylonitrile forms explosive mixtures with air within the limits of 3.0-17.0 percent (by volume). The chief outlet of acrylonitrile is as a monomer for the production of synthetic fibres—polyacrylonitrile (nitron), copolymers with methacrylate (acrylon), with vinyl chloride (vinylon N), etc., plastics (copolymers with styrene), synthetic rubber (a copolymer with butadiene), etc. Besides, acrylonitrile is an intermediate for the synthesis of acrylates and acrylamide and also for the introduction of the β -cyanoethyl group into organic compounds.

The first commercial method of acrylonitrile production was the synthesis from ethylene oxide and HCN:



Later, acrylonitrile was produced from acetylene and HCN:

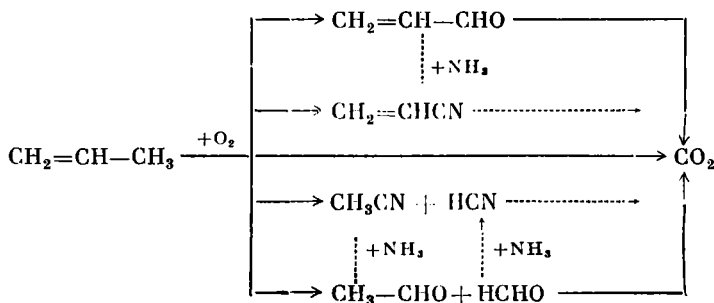


Both these methods have been superseded by the oxidative ammonolysis of propylene, which makes use of the cheaper raw material.

Oxidative Ammonolysis of Propylene. The catalysts used for the oxidative ammonolysis of propylene are similar to those used for the oxidation of propylene to acrolein. The original developments were based on bismuth molybdate ($\text{Bi}_2\text{O}_3 : \text{MoO}_3 = 1 : 2$), promoted with phosphorus pentoxide (bismuth-phosphorus-molybdenum catalysts). Good results are also obtained by using bismuth vanadium-molybdates, oxide uranium-antimony catalysts, etc. There are also catalysts with a large number of components, containing added amounts of the oxides of Co, Ni, Fe, As, W, Te and other metals and rare-earth elements. These catalysts are used either in pure form or supported on SiO_2 , Al_2O_3 and diatomaceous earth.

All these catalysts function according to the redox mechanism outlined above, and the reaction rate depends only on the partial pressure of propylene ($r = kP_{\text{C}_3\text{H}_6}$), indicating that the rate-limiting step is the interaction of propylene with the oxidized active centre of the catalyst, where the chemisorbed allyl radical is formed. Ammonia is sorbed on another active centre, probably in the form of the imine radical :NH . It is their interaction with each other (in which the lattice oxygen takes part) that results in the formation of acrylonitrile.

The by-products of the oxidative ammonolysis of propylene are HCN, CH_3CN , and also HCHO and CH_3CHO formed in small amounts (these are formed as a result of the oxidative degradation of propylene); carbon dioxide is also formed. Nitriles were believed to be formed via the intermediate aldehyde step, but today there is evidence that they are mainly formed in a parallel reaction. The most probable scheme of conversions involved in the oxidative ammonolysis of propylene is as follows:



Thus, carbon dioxide results from the oxidation of all the components of the mixture, but the major proportion is formed from pro-

pylene. In contrast to propylene and aldehydes, the complete oxidation of nitriles occurs under reaction conditions with a low velocity, which is why the selectivity must depend little on the degree of conversion.

The process of oxidative ammonolysis of propylene was originally carried out in tubular reactors containing a fixed catalyst bed, but today fluidized-bed reactors are employed. This provided a better temperature control, removed the limitation imposed by the explosion hazard of the feed mixture and eliminated the need for the dilution of the mixture with steam. The oxidation is effected using air, the volume ratio of $C_3H_6 : NH_3 : O_2$ being maintained within the limits of 1 : (0.9-1.1) : (1.8-2.4). It is important that the mixture leaving the reactor contain unreacted ammonia, since otherwise the yield of aldehydes and carbon dioxide will increase. A certain excess of oxygen is also required; together with propylene and ammonia the oxygen provides the redox properties of the medium, which are favourable for the increase of the activity and selectivity of the catalyst.

Depending on the plant and the catalysts used, the oxidative ammonolysis of propylene may be accomplished at 370-500 °C and 0.2-1.4 MPa; in most cases it is carried out at 420-470 °C and 0.2 MPa. The contact time is ≈ 6 s, in which case the degree of conversion of propylene amounts to 80 percent (in one of the new processes, the conversion is said to be as high as 95 percent). The propylene fraction may contain 5-40 percent of propane, which reduces its cost. The selectivity of the process with respect to acrylonitrile under the conditions indicated above is 80-85 percent; the hydrogen cyanide and acetonitrile formed as by-products are commercial products; this reduces the cost of acrylonitrile. Depending on the plant, the yield of HCN and acetonitrile may be 50-200 and 25-100 kg per 1 ton of acrylonitrile.

In the latest flow diagrams of acrylonitrile production use is made of an efficient heat utilization system with generation of steam (high- and medium-pressure steam), which satisfies all the needs of the plant (it is used to drive the air compressor, to separate the mixtures, etc.). One of these flow diagrams is shown in Fig. 6.26.

Liquid ammonia and propylene fraction are evaporated in vaporizers 1 and 2 using ethylene glycol (EG) with water; the mixture cools down to lower temperatures, and its cold is utilized for various purposes (including the condensation of hydrogen cyanide). The gaseous ammonia, propylene fraction and air in the ratio mentioned above are passed to reactor 3 with a fluidized catalyst bed. The reactor is cooled by the boiling water condensate. The reaction heat is used to produce high-pressure steam, which is used to drive the air turbocompressor, and the spent steam leaving the compressor is used at the product separation stage. The hot gases leaving the reactor

pass through waste-heat boiler 4, where medium-pressure steam is generated.

The partially cooled reaction gases are first purified from ammonia in absorber 5 with the aid of the circulating solution of ammonium sulphate containing sulphuric acid. The ammonium sulphate solution spent in the absorber is evaporated and crystallized, as a result

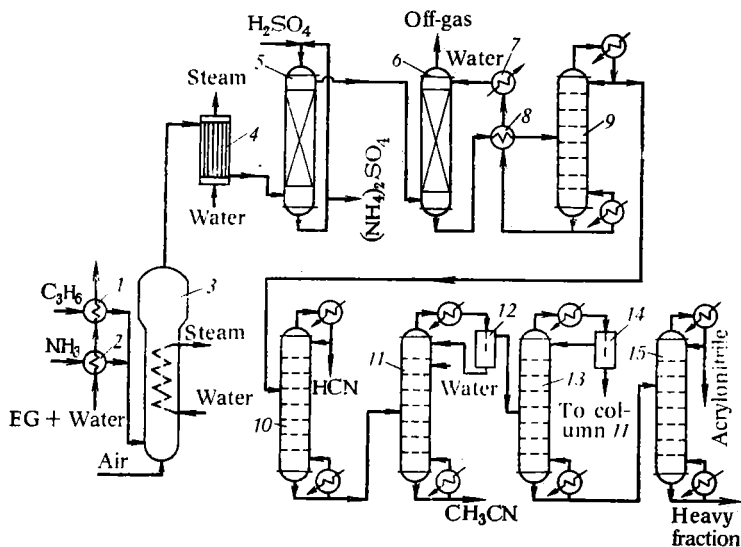


Fig. 6.26. Flow diagram of acrylonitrile production:

1, 2—vaporizers; 3—reactor; 4—waste-heat boiler; 5, 6—absorbers; 7—cooler; 8—heat exchanger; 9—stripping column; 10, 15—fractionating columns; 11—extractive-distillation column; 12, 14—separators; 13—azeotropic-drying column.

of which ≈ 400 kg of $(\text{NH}_4)_2\text{SO}_4$ is obtained per 1 ton of acrylonitrile. Then, acrylonitrile, hydrogen cyanide and acetonitrile are absorbed from the gas in absorber 6 by water, and the effluent gas is either discharged into the atmosphere or burned in the furnace to produce steam, depending on the composition.

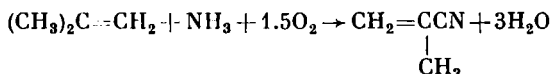
The aqueous solution of products from the bottom of absorber 6 is heated in heat exchanger 8 by recycle water and passed into stripping column 9 fitted with a boiler and a dephlegmator, where hydrogen cyanide, acrylonitrile and acetonitrile are separated from water. The water is returned through heat exchanger 8 and cooler 7 to absorber 6 and the mixture of products is sent to separation.

Commonly, the most volatile hydrogen cyanide is distilled off first from the mixture in fractionating column 10 equipped with a boiler and a dephlegmator in a low vacuum (in order to prevent the discharge of highly toxic HCN into the atmosphere). The more vola-

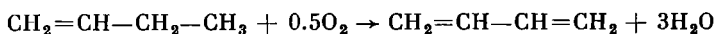
tile azeotropic mixture of acrylonitrile is distilled off from the still liquid in column 11 with water as a third component, the aqueous solution of acetonitrile with an impurity of the less volatile compounds (cyanohydrins, formaldehyde and acetaldehyde formed from these aldehydes and HCN) being left in the still. Then, acetonitrile is separated from the solution (not shown in the flow diagram). The distillate is separated in separator 12 into an aqueous and an organic layer, the water being returned to column 11.

The aqueous acrylonitrile is subjected to azeotropic drying in column 13 fitted with a boiler, a dephlegmator and separator 14, where the aqueous and acrylonitrile layers are separated. The aqueous layer is returned to column 11, since it contains the dissolved acrylonitrile, and the acrylonitrile layer is used to reflux column 13. The dry acrylonitrile is collected in the still of column 13 and subjected to final fractionation in column 15 to produce a distillate of the required purity. At the product separation stage, inhibitors are added to the mixture in order to avoid polymerization of acrylonitrile.

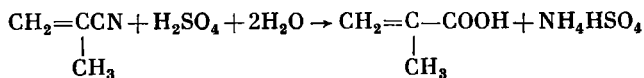
Methacrylonitrile can be obtained from isobutylene, ammonia and air in the same way as acrylonitrile:



It has been observed that, just as in the synthesis of methacrolein (page 453), methacrylonitrile is obtained with a higher selectivity when the butylene fraction is subjected to oxidative ammonolysis without being separated into the isomers. Under these conditions, *n*-butylenes undergo oxidative degradation with the highly selective formation of butadiene:



Methacrylonitrile is a cheaper raw material than acetone cyanohydrin for the synthesis of methacrylates, but in this case too sulphuric acid is consumed and ammonium bisulphate is formed:

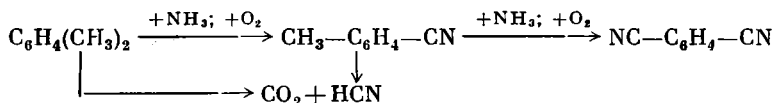


Therefore, the synthesis of methacrylonitrile is not in much favour, and major attention is focused on the oxidation of isobutylene outlined above.

Oxidative Ammonolysis of Methylbenzenes. This process is mainly used for the synthesis of the dinitriles of isophthalic and terephthalic acids (phthalonitriles) from *m*- and *p*-xylenes or their mixtures. Terephthalonitrile has been proposed as an intermediate for the synthesis of high-purity terephthalic acid. Isophthalonitrile is employed for the manufacture of *m*-xylylenediamine—a monomer

for the synthesis of thermally stable polyamides, xylylene diisocyanates and polyurethanes based on these diisocyanates, etc.

The oxidative ammonolysis of the xylenes proceeds stepwise and is accompanied by the formation of by-product CO_2 and hydrogen cyanide:



The intermediate tolunitrile can be isolated from the mixture and returned to oxidative ammonolysis. The most effective catalysts for this process are mixtures of the oxides of vanadium and chromium, vanadium and molybdenum, and vanadium, titanium and bismuth. The reaction is carried out at 350–480 °C and atmospheric pressure in reactors containing a fixed or fluidized catalyst bed with a contact time of 1–2 s. In contrast to the synthesis of acrylonitrile, use is made of a considerable excess of ammonia and oxygen (in the form of air) with respect to the xylene—a two- or threefold excess with respect to the stoichiometric amount.

The reaction unit for this process is the same as for the synthesis of acrylonitrile, but the separation of the products differs significantly because of the differences in their properties. In this particular case, the low-volatile nitriles are separated first, following which the ammonia is isolated from the reaction gases, the residual gas being sent to burning. The production of phthalonitriles has been realized industrially in a number of countries and is being further improved.

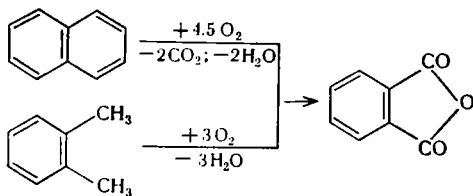
6.3.4. Production of Phthalic, Maleic and Other Cyclic Anhydrides

The gas-phase heterogeneous-catalytic oxidation of hydrocarbons has assumed great industrial significance for the synthesis of the anhydrides of di- and tetracarboxylic acids, which exhibit high thermal-oxidation stability (maleic, phthalic and other anhydrides).

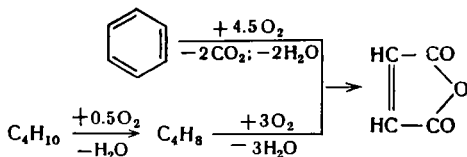
Phthalic anhydride is the most important representative. It is a solid crystalline substance (m.p. 130.8 °C; subl. p. 284.5 °C). The chief outlet of phthalic anhydride is in the production of alkyd resins by its polycondensation with glycerine, pentaerythritol and other polyhydric alcohols.

The esters of phthalic acid with C_4 – C_8 alcohols are widely employed as plasticizers for polymeric materials and its methyl and ethyl esters find use as preparations for scaring off blood-sucking insects. Lesser quantities of phthalic anhydride are used in the manufacture of dyes.

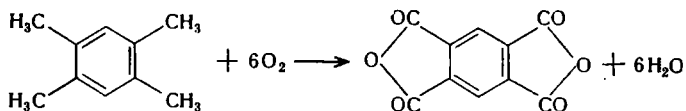
The main route to phthalic anhydride has been the oxidation of naphthalene, but an ever increasing use is made for this purpose of less expensive *o*-xylene:



Maleic anhydride is a crystalline substance (m.p. 52.8 °C; b.p. 200 °C). It is soluble in water and is hydrolyzed by it to maleic acid. The latter when heated is capable of being isomerized to fumaric acid (the *trans*-isomer), a fact which should be taken into account in the production of maleic anhydride. Maleic anhydride has a number of important outlets, but it is primarily used for the synthesis of unsaturated polyesters. The principal method of its production is the gas-phase oxidation of benzene with air, but at present more available butylenes and even butane find an ever increasing use as the feedstock:



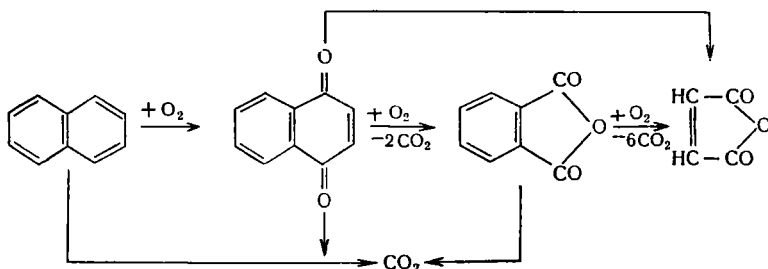
Pyromellitic dianhydride has recently found application for the synthesis of thermally stable polymers of the type of polyimides, which are produced by the polycondensation of pyromellitic dianhydride with aromatic diamines. Pyromellitic dianhydride is obtained by the gas-phase oxidation of durene over vanadium pentoxide, but the yield is less than 50 percent:



Typical catalysts for all these processes are compositions based on vanadium pentoxide, which, in contrast to molybdates used for the oxidation and oxidative ammonolysis of olefins, are typically used for the disruptive oxidation of organic compounds. Various oxides (TiO₂, MoO₃) and also sulphates and phosphates are added to the catalyst to increase its activity and selectivity.

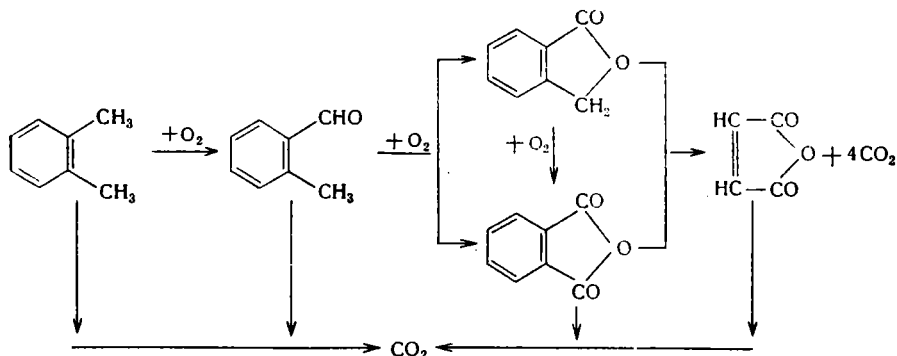
6.3.4.1. Production of Phthalic Anhydride

The production of phthalic anhydride from naphthalene involves the following scheme of conversions:



Phthalic anhydride is relatively stable to further oxidation and the reaction is therefore carried out practically to complete conversion of naphthalene. The yield of 1,4-naphthoquinone and maleic anhydride is so low that it is not profitable to isolate them from the mixture obtained, and the major side process is the oxidation to CO_2 . The most effective catalyst for the oxidation of naphthalene is V_2O_5 with an added amount of K_2SO_4 on silicagel; with this catalyst the yield of phthalic anhydride is ≈ 90 percent at $360-400^\circ C$.

The following conversions take place during the oxidation of *o*-xylene:



Here, with a practically complete conversion of *o*-xylene the selectivity with respect to phthalic anhydride is found to be much lower, and the yield of maleic anhydride is 5-8 percent; in large plants it is profitable to separate it from the resultant mixtures in the form of a commercial product. The best catalyst for the oxidation of *o*-xylene is an oxide vanadium-titanium catalyst, with which the yield of phthalic anhydride reaches 70-75 percent at $370-400^\circ C$. In spite of

the lower yield of phthalic anhydride, the scale of its production from less expensive *o*-xylene increases.

Technologically, the oxidation of naphthalene is analogous to the oxidation of *o*-xylene and there are plants which combine the processing of both raw materials. The process is carried out at atmospheric pressure and with a large excess of air, which provides a reactant concentration of 0.7-0.9 percent (by volume); this is outside the explosive limits of the mixture with air. The reaction units most often used for this process are multi-tube reactors with a fixed catalyst

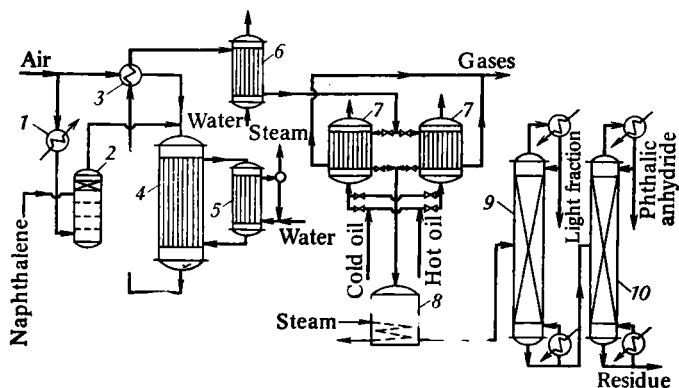


Fig. 6.27. Flow diagram of production of phthalic anhydride from naphthalene: 1—preheater; 2—vaporizer; 3, 6—heat exchangers; 4—reactor; 5—waste-heat boiler; 7—condensers; 8—tank; 9, 10—fractionating columns.

bed, which are cooled by the boiling water condensate or, more frequently, by a nitrite-nitrate mixture with the generation of steam. Much attention has lately been devoted to the effective utilization of heat, the amount of which is enough to satisfy all the needs of the plant; part of the steam generated (up to 3.6 tons per 1 ton of phthalic anhydride) is used for other purposes.

One of the flow diagrams of the production of phthalic anhydride from naphthalene is given in Fig. 6.27. Molten naphthalene is fed at $\approx 100^\circ\text{C}$ into vaporizer 2 fitted with several cap plates. Part of the air (preheated in heater 1) is also admitted into vaporizer 2. The air becomes saturated with naphthalene vapours to a concentration of 8-10 percent, which exceeds the upper explosive limit. The remaining amount of air is heated in heat exchanger 3 by the hot reaction gas and is mixed with the air saturated with naphthalene vapours, and the mixture is led into tubular reactor 4.

The reactor is cooled with the circulating salt melt; high-pressure (up to 5 MPa) steam is generated in waste-heat boiler 5. This steam is used to drive the turbocompressor which supplies air for oxidation; some of the spent steam from the turbine is partly used at the same

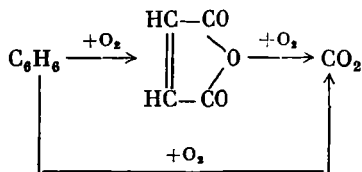
plant, the remainder being utilized for other purposes. The hot reaction gases give off their heat to the air in heat exchanger 3 and are then cooled in heat exchanger 6, where (depending on the plant) either low-pressure steam is produced or the water condensate is heated and then passed to waste-heat boiler 5.

The cooled reaction gases pass then into a system of two alternately operating condensers 7 with oil-cooled finned tubes. The phthalic anhydride is deposited on the tubes in the solid form; when a sufficient amount of phthalic anhydride is accumulated, the gas stream is led into the second condenser, and the first is heated by the hot oil. The molten phthalic anhydride flows from the condenser into intermediate tank 8, from which it is led for purification to a system of two vacuum-fractionation columns 9 and 10. In column 9 the more volatile compounds are distilled off, and pure phthalic anhydride is drawn off as the distillate from column 10. The light distillate from column 9 and the heavy still residue from column 10 are burned.

The residual gas leaving cooler 7 (in the synthesis of phthalic anhydride from naphthalene) is completely burned up in the furnace; in the production of *o*-xylene, the gas is first passed through the absorber refluxed by water, where maleic anhydride is absorbed. The maleic anhydride is here hydrolyzed to maleic acid, which is converted to the anhydride by the methods described below. Another distinctive feature in the flow diagram of the production of phthalic anhydride from *o*-xylene is that no naphthalene vaporizer is used and the air is not separated into two streams. Instead, the airstream mixture is produced in a mixer.

6.3.4.2. Production of Maleic Anhydride

The major proportion of maleic anhydride is produced by the heterogeneous-catalytic oxidation of benzene, the only by-product being carbon dioxide. It is formed both from benzene and maleic anhydride:

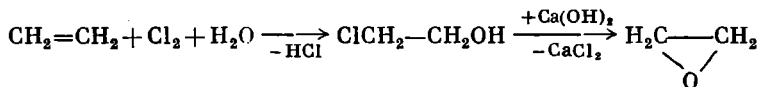


Further oxidation of maleic anhydride proceeds relatively slowly, which is why the process is carried to an almost complete conversion of benzene.

The best catalyst for the oxidation of benzene is a mixture of the oxides of vanadium and molybdenum usually supported on large-pore Al_2O_3 . The catalyst is often modified by the oxides of phosphorus, titanium and boron. The optimum temperature range is 350-

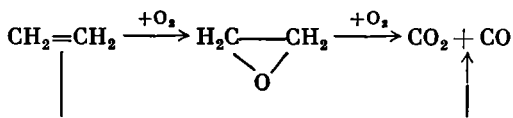
Ethylene oxide is one of the most important intermediates of organic synthesis; it is produced on a large scale and is widely used for the synthesis of numerous compounds (page 297).

The earliest method to become established for the production of ethylene oxide used ethylene chlorohydrin as an intermediate product: (page 134):



This method involves the consumption of large quantities of chlorine and alkali and also the formation of salt wastes and, on this account, it has been replaced by a direct oxidation (epoxidation) of ethylene.

In spite of the absence of saturated carbon atoms in ethylene, the direction of its oxidation may vary, depending on the process parameters and the catalyst used. The choice of the catalyst selective enough with respect to the oxidation of ethylene to ethylene oxide was made in the thirties. It was found that metallic silver deposited onto various supports acts selectively at moderate temperatures—within the range of 200–300 °C. The same catalyst causes at a higher temperature the complete oxidation of ethylene; at a lower temperature it becomes deactivated. When the silver catalyst is used, of all the possible routes there predominantly occur the formation of ethylene oxide and the complete oxidation of ethylene; acetaldehyde is formed in small amounts as a result of an isomerization reaction. It has been found that CO_2 is formed both from ethylene and ethylene oxide; the rate of the oxidation of the α -oxide is sufficiently high, this being responsible for a considerable decrease in selectivity with increasing degree of conversion of ethylene:



Numerous modifications of the silver catalyst have been proposed for the oxidation of ethylene. The supports proposed include pumice, silicagel, aluminium oxide, mixtures of silicagel and aluminium oxide, and silicon carbide. Antimony, bismuth, and barium peroxide have been recommended as the promoters and also as the additives that increase the selectivity of the catalyst. It is interesting that the addition of a small amount of deactivating impurities (sulphur, the halogens) increase the selectivity of the silver catalyst; the best way is to add these substances continuously to the reaction mixture, compensating for its consumption on the oxidation. It has been found that the addition of 0.01–0.02 mass. p. of dichloroethane per 1 mass. p.

of ethylene: the selectivity of the process increases in this case by about 5 percent.

The selectivity is also influenced by the temperature. It has been observed that the complete oxidation has a higher activation energy, which is why at a constant degree of ethylene conversion the selectivity falls off with increasing temperature (see Fig. 6.23a). The optimum temperature range is 220-280 °C, but the decrease of temperature, which is favourable for selectivity, results in a decrease in the catalyst capacity. This effect is compensated by carrying out the

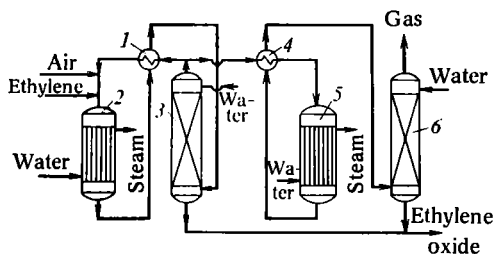


Fig. 6.28. Flow diagram of production of ethylene oxide by the air oxidation of ethylene:

1, 4—heat exchangers; 2, 5—reactors; 3, 6—absorbers.

process at a pressure of 1-3 MPa, which has no effect on the selectivity and facilitates the absorption of volatile ethylene oxide from the reaction gases.

Since the selectivity depends significantly on the degree of conversion of ethylene, tubular reactors have proved to be most suitable for the process (see Fig. 6.24a); these reactors are cooled by the boiling water condensate under pressure or by the intermediate heat-transfer agent that produces steam in a special steam generator. The use of reactors containing a fluidized catalyst bed gives poorer results and has therefore been abandoned.

Air Oxidation of Ethylene. The reaction was the first variant of the synthesis of ethylene oxide; it is still in much favour at present. A simplified flow diagram of the process is shown in Fig. 6.28. The oxidation is effected successively in two tubular reactors 2 and 5 with the intermediate absorption of ethylene oxide from the reaction gases after the first step. This provides the possibility (which is specific to this process) of reducing the further oxidation of the α -oxide with an increase in the degree of ethylene conversion and, hence, it becomes possible to raise the selectivity of the process. Moreover, it makes it possible to effect the circulation of the gas at the first oxidation step, which leads to a more complete utilization of ethylene and oxygen and reduces the explosion hazard owing to the dilution by nitrogen and carbon dioxide.

Before fresh air and ethylene are led to the first oxidation step they are mixed with the recycle gas from this step. The gas from the top of absorber 3 (after it is compressed to the operating pressure) is preheated in heat exchanger 1 by the gas from reactor 2. The mixture entering reactor 2 contains 4-6 percent (by volume) of ethylene, 6-8 percent of oxygen and 8-10 percent of carbon dioxide, the remainder being nitrogen and inert impurities from the ethylene feed.

The process in the first reactor is carried out at a contact time of 1-4 s and 30-40 percent conversion of ethylene; the gas leaving the reactor contains 1.5 percent (by volume) of ethylene oxide. The heat of the gas is used in heat exchanger 1, and after being additionally cooled it is sent to first-stage absorber 3, where the ethylene oxide is absorbed by water. The gas leaving the absorber is separated into two streams: the major proportion is returned to the first oxidation step, the remaining part being led to additional oxidation through heat exchanger 4 to reactor 5.

Since the second-stage gas is discharged into the atmosphere, the operating conditions chosen in reactor 5 must provide the maximum yield of ethylene oxide, i.e., the process is carried out with a considerable conversion of the ethylene and with a slightly reduced selectivity. The second-stage gas, just as the gas from the first step, is cooled in heat exchanger 4 and led to second-stage absorber 6, where the ethylene oxide is absorbed. The gas leaving this absorber is discharged into the atmosphere and the solutions of ethylene oxide (and CO_2) from absorbers 3 and 6 are processed jointly to obtain the product in pure form. The total yield of the α -oxide is 60 percent on ethylene at an average selectivity of about 65 percent, the overall degree of ethylene conversion being ≈ 90 percent.

The added feature in plants of this type that have been constructed only recently is the circulation of the gas after the second oxidation step; with a large-capacity plant it is profitable to effect a three-step oxidation with the circulation of the gas after each step. The maximum yield of ethylene oxide attainable by using this method is 65 percent.

Oxidation of Ethylene by Oxygen. This method is a new and very promising method of synthesis of ethylene oxide. Despite the use of a more expensive reactant, oxygen, this method has a number of advantages: the oxidation selectivity is increased up to 70-75 percent; the loss of ethylene with the effluent gas diluted with the air nitrogen is lowered; the size of the vessels is reduced.

When ethylene is oxidized by oxygen, the gas is also recycled after the ethylene oxide is absorbed from it; the reaction is effected in an excess of ethylene with respect to oxygen, the ethylene conversion being ≈ 10 percent per pass through the reactor. The content of inert impurities in ethylene and oxygen is insignificant and for the composition of the mixture to be maintained constant only a small

part of the gas must be blown off, which permits the use of a single reactor. However, because of the formation of carbon dioxide the recycle gas must be purified from CO_2 in order to maintain its concentration in the recycle constant.

The flow diagram of the synthesis of ethylene oxide by the oxidation of ethylene with oxygen is given in Fig. 6.29. The recycle gas is compressed to the operating pressure (≈ 2 MPa), heated in heat exchanger 2 by the hot reaction gas and mixed with fresh ethylene

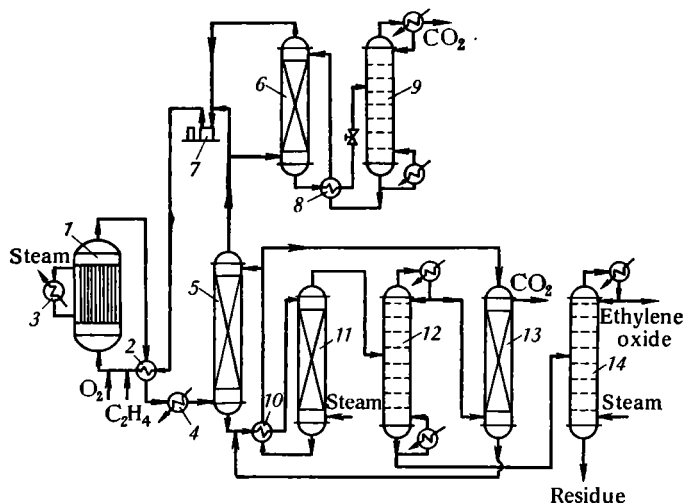
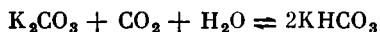


Fig. 6.29. Flow diagram of production of ethylene oxide by oxidation of ethylene by oxygen:

1—reactor; 2, 8, 10—heat exchangers; 3—steam generator; 4—cooler; 5, 6, 13—absorbers; 7—circulation compressor; 9—desorber; 11—stripping column; 12, 14—fractionating columns.

and oxygen. The resultant mixture introduced into reactor 1 contains 20-30 percent (by volume) of ethylene, 7-8 percent of oxygen and 4-5 percent of CO_2 ; it also contains inert impurities (N_2 , Ar, etc.) from the gas feed. The oxidation is effected in tubular reactor 1 cooled by the intermediate heat-transfer agent; steam of ≈ 2 MPa pressure is produced in steam generator 3. The hot reaction gases containing 1.8-2 percent (by volume) of ethylene oxide are cooled in heat exchanger 2, cooler 4 and transferred to absorber 5, where all of the ethylene oxide and part of CO_2 are absorbed by water. The gas leaving the absorber is separated into two streams; one stream is recycled and the other is sent to absorber 6, where it is purified from CO_2 by aqueous potassium carbonate:



The carbonate absorbs CO_2 from the gas in the cold under pressure and the purified gas is returned to the reactor after being compressed to the operating pressure by compressor 7. The solution obtained in the absorber is heated in heat exchanger 8 by the countercurrent absorbent stream, throttled and run to desorber 9, where CO_2 is removed on heating. The regenerated absorbent is pumped through heat exchanger 8 to absorber 6.

The aqueous solution of ethylene oxide and CO_2 from the still of absorber 5 is throttled up to 0.5 MPa and is led through heat exchanger 10 to stripping column 11, where ethylene oxide, CO_2 and part of the water are distilled off. The major amount of water is left in the still and then returned to absorber 5 after being cooled in heat exchanger 10. The vapours leaving stripping column 11 are sent to fractionator 12, where CO_2 and part of ethylene oxide distill out. The oxide is absorbed from the gas by water in absorber 13, the aqueous solution being returned to column 11. The still liquid of column 12 passes to fractionator 14, where pure ethylene oxide is obtained.

The production of ethylene oxide by this method is highly economical and has many advantages as compared with the method based on the use of air. It employs an effective heat utilization system and no toxic wastes are discharged into the environment. Not infrequently, this process is combined with the production of ethylene glycol into a single technological system, which adds to the economy of the process. The carbon dioxide obtained as a by-product can be used for the production of carbamide or dry ice.

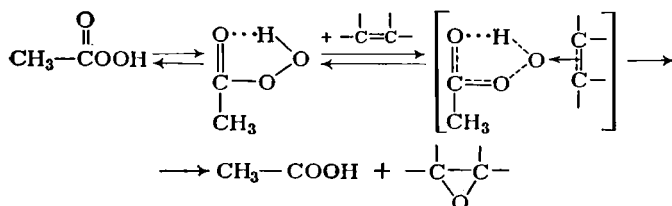
6.4. Oxidation of Olefins Catalyzed by Metal Complexes

These processes are new in the oxidation technology; there are two groups of processes:

- (1) epoxidation of unsaturated compounds with the manufacture of α -oxides or products of their further conversions;
- (2) oxidation and oxidative coupling of olefins with the formation of carbonyl compounds, esters or other compounds.

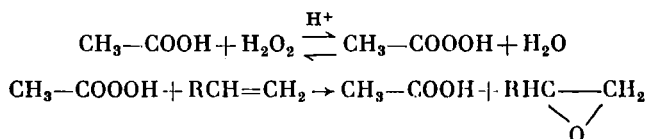
The products obtained (propylene oxide and other α -oxides, acetaldehyde, vinyl acetate) are valuable intermediates or monomers; the oxidative methods of their manufacture have proved to be economically the most effective. This has given an impetus to the rapid development and commercial application of metal-complex catalysis of oxidation processes.

The reaction is carried out in a solvent at 30-50 °C when further addition of the carboxylic acid with the opening of the α -oxide ring is not yet significant. It is believed that the peracid reacts in a cyclic form with an intramolecular hydrogen bond, when a partial positive charge appears on the peroxide oxygen atom; this charge makes possible the electrophilic attack of the double bond:

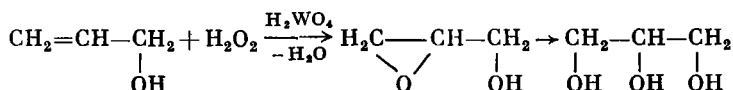


The epoxidation by peracetic acid has been applied until recently only in fine organic synthesis, but an industrial plant has been reported, which is designed for the synthesis of propylene oxide from propylene and peracetic acid, the acid being obtained by the oxidation of acetaldehyde.

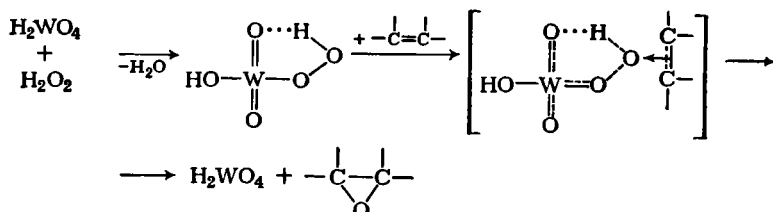
A modified method of epoxidation across the double bond consists of the use of peracetic acid synthesized directly in the reaction mixture from acetic acid and hydrogen peroxide upon acidic catalysis. Since the α -oxides are sensitive to the action of acids, this method yields good results only when it is realized in a system composed of two phases (an aqueous and an organic phase), when the peracid formed in the aqueous phase passes over into the organic phase and, epoxidizes there the water-insoluble unsaturated organic compound:



Another method has been developed for the epoxidation of water-soluble compounds containing a double bond (primarily, allylic alcohol and acrolein), which is based on the use of a solution of hydrogen peroxide and which is catalyzed by tungstic acid, H_2WO_4 . It commonly involves the subsequent hydration of the α -oxide for the production of glycerine:

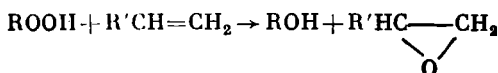


The mechanism of the reaction involves the formation of pertungstic acid, H_2WO_5 , which reacts with the olefin in its cyclic form in the same way as organic peracids:



6.4.1.2. Epoxidation by Hydroperoxides

The use of organic hydroperoxides for the synthesis of α -oxides failed to give good results for a long time and only in the early sixties did it become possible to obtain satisfactory results through the use of metal-complex catalysts in the liquid phase:



The catalysts used for the reaction are the salts and various complexes (acetyl acetonates, carbonyls) of molybdenum, tungsten, vanadium, titanium, niobium and other transition metals soluble in the reaction mass. The rate and selectivity of the reaction depend strongly on the nature of the metal and the form in which it is used. This is illustrated below for the reaction between ethylbenzene hydroperoxide and propylene catalyzed by metal naphthenates:

Metal	Conversion at 100 °C for 1 hour, %	Selectivity, %
Mo	97	71
W	83	65
Ti	54	55
Nb	22	20
Ta	25	23
Re	100	10

Of these catalysts, only molybdenum naphthenate, with which the velocity and selectivity of the process are sufficiently high, and other compounds of molybdenum are used in the industry of organic synthesis.

The nature of the hydroperoxide also has a substantial effect on these process parameters. For example, if the reaction of the hydroperoxide with propylene is catalyzed by molybdenum naphthenate, 92 percent of ethylbenzene hydroperoxide, 79 percent of isopropylbenzene hydroperoxide and only 29 percent of isopentane hydroperoxide will react at 100 °C in 15 min. The selectivity of the process

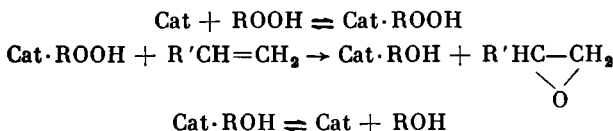
varies in the same order under the conditions of the equal degree of conversion. The choice of the hydroperoxide is dictated, however, not only by these factors but also by the practical value of the second product—the alcohol, which can be converted to the corresponding olefin by dehydration. The ethylbenzene, isobutane and isopentane hydroperoxides are superior in all these respects to other hydroperoxides and have assumed a dominant position in industrial practice.

An important role is played by the structure of an unsaturated compound, its reactivity being increased by the presence of electron-releasing substituents. Propylene, other ethylene homologues and styrene are readily epoxidized; ethylene and especially allyl chloride are epoxidized with difficulty.

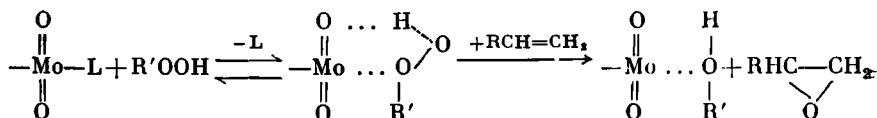
The study of the reaction kinetics has demonstrated that in many cases there is an induction period, during which an active catalyst complex is formed. It has been observed that the reaction is retarded by a number of compounds, including the products formed, this being characteristic of metal-complex catalysis. Under steady-state conditions the reaction velocity is proportional to the concentrations of the catalyst, hydroperoxide and olefin, and the kinetic equation is as follows:

$$r = k \frac{C_{\text{cat}} C_{\text{hydr}} C_{\text{olef}}}{1 + K_1 C_{\text{hydr}} + K_2 C_{\text{ROH}}}$$

It corresponds to the following scheme of the process:



It is presumed that the role of the catalyst is to activate the hydroperoxide molecule, which coordinates by its oxygen atom with the central metal ion, which is in one of the higher valence states (Mo^{6+} , etc.). The olefin reacts with the resultant complex:



Since the principal side reaction is the parallel decomposition of the hydroperoxide ($\text{ROOH} \rightarrow \text{ROH} + 0.5\text{O}_2$), which also takes place on the catalyst, the differential selectivity of the reaction with respect to the hydroperoxide is approximately equal to:

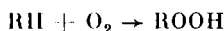
$$\varphi = \frac{1}{1 + \frac{r_2}{r_1}} = \frac{1}{1 + \frac{k_2}{k_1 C_{\text{olef}}}}$$

Its increase is favoured by a high concentration of the unsaturated compound (this requires a high pressure for the reaction with gaseous olefins) and a moderate temperature (since the activation energy of epoxidation is lower than that of the decomposition of hydroperoxide). Since the ratio k_2/k_1 is reduced, the selectivity is always higher in the epoxidation of more reactive unsaturated compounds and when use is made of hydroperoxides which are more stable to decomposition. In contrast to this, the selectivity of the process with respect to the olefin is high, being close to 100 percent.

The regularities of the reaction considered above dictated the choice of its conditions. The process is carried out in the liquid phase (usually, in a solution of the hydrocarbon from which the hydroperoxide was obtained), at 90-110 °C and with a 2-5-fold excess of the olefin with respect to the hydroperoxide. Depending on the volatility of the hydrocarbon-solvent and olefin, the pressure required to maintain the liquid state of the reaction mass varies from 5 to 7 MPa. Under these conditions the reaction has a sufficiently high selectivity with the amount of the catalyst being 0.001-0.005 mole per 1 mole of hydroperoxide, which allows the catalyst regeneration to be dispensed with. Depending on the temperature, the catalyst concentration and the nature of the reactants, the reaction time varies from 0.3 to 2 hours.

The reaction of hydroperoxides with olefins gives two major products—an α -oxide and an alcohol; the latter can be dehydrated to the corresponding olefin, which is why all processes of this type are combined and proceed, as a rule, in three steps:

1. The oxidation of a suitable hydrocarbon (ethylbenzene, isobutane, isopentane) to a hydroperoxide:



The mechanism and conditions of this reaction have been considered earlier (page 397); the by-products formed are the corresponding alcohol and ketone. The separation of the hydroperoxide in concentrated form has proved to be inexpedient, and it is "strengthened" only to a concentration of 20-30 percent, the starting hydrocarbon being used as a solvent for the epoxidation.

2. The epoxidation of the unsaturated compound with the formation of the α -oxide and alcohol under the conditions indicated above.

3. The dehydration of the alcohol to the corresponding olefin (styrene, isobutylene, isoamylene); the mechanism of the process has already been described (page 209).

This combined process has come to be known as the *Halcon process* after the name of the firm that developed it.

Technology of the Combined Synthesis of Propylene Oxide and Styrene (or Propylene Oxide and Isobutylene). The Halcon process

This mixture is neutralized with caustic (not shown in the flow diagram) and then subjected to fractional distillation in column 5 to isolate the most volatile ethylbenzene, which is recycled to the synthesis of the hydroperoxide. The still residue of column 5 passes to vaporizer 6, where the phenyl methyl carbinol and acetophenone are vaporized in a current of superheated steam and are separated from the resins. The mixture of vapours heated in heat exchanger 7 up to 300 °C passes successively through two reactors 8 filled with a

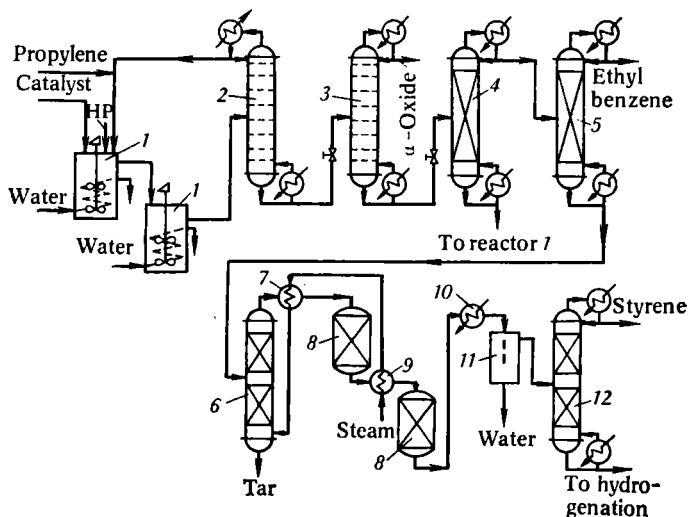


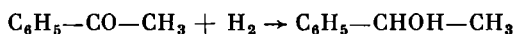
Fig. 6.30. Flow diagram of production of propylene oxide and styrene by the Halcon method:

1—epoxidation reactors; 2, 3, 4, 5, 12—fractionating columns; 6—vaporizer; 7, 9—heat exchangers; 8—dehydration reactors; 10—cooler; 11—separator.

heterogeneous acid-type catalyst and is subjected to dehydration. This reaction is endothermic, which is why the mixture cooled after the first reactor 8 is heated by steam in heat exchanger 9. The overall degree of conversion of phenyl methyl carbinol upon dehydration is 90 percent.

The resultant vapours are cooled and condensed in cooler 10, following which the aqueous layer is separated from the organic layer in separator 11. The water is again passed for the preparation of the steam-diluent, thereby forming a closed water circuit system. The organic layer contains styrene, acetophenone and unconverted phenyl methyl carbinol. The styrene is distilled off from this mixture in column 12 and additionally purified with the recovery of the product of the monomer purity (not shown in the flow diagram). The acetophenone and traces of phenyl methyl carbinol are left in the

still of column 12. They are led to the hydrogenation unit, where the acetophenone is converted to phenyl methyl carbinol:

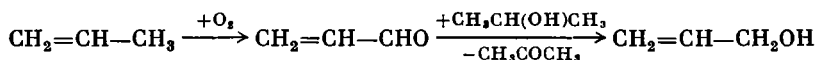


The hydrogenation product is returned to the dehydration step.

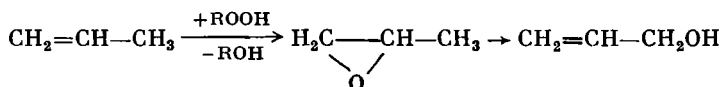
The selectivity of the conversion of propylene to the α -oxide amounts to 95-97 percent. The selectivity based on the hydroperoxide at the steps of its synthesis and epoxidation is 80-85 percent, but owing to the efficient use of the by-products of ethylbenzene oxidation and hydroperoxide decomposition (phenyl methyl carbinol and acetophenone) the yield of styrene reaches 90 percent based on ethylbenzene. There are formed 2.6-2.7 tons of styrene per 1 ton of propylene oxide.

The Halcon process gave an impetus to the development of a number of other combined methods of synthesis; some of these will be described below.

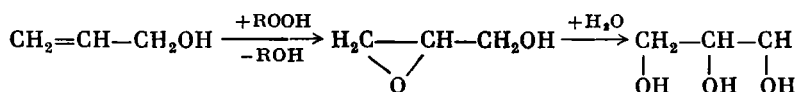
Oxidative Methods of Glycerine Synthesis. These methods have been worked out specifically for the replacement of the chlorine method of glycerine production (page 192), which involves the consumption of large quantities of chlorine and alkali and the formation of salt wastes. The new methods use propylene as the feedstock. Propylene can be oxidized to acrolein (page 450) and the latter reduced to allyl alcohol by way of the catalytic redistribution of hydrogen with isopropyl alcohol:



On the other hand, allyl alcohol can be prepared by the isomerization of propylene oxide (synthesized by the hydroperoxide epoxidation of propylene) over the heterogeneous catalyst LiHPO_4 at 200 °C:



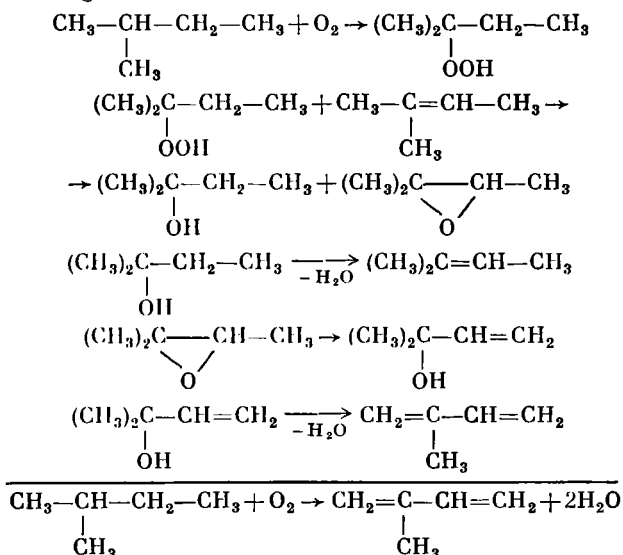
Allyl alcohol can then be epoxidized not only by a peracid or hydrogen peroxide (page 470) but also by a hydroperoxide in the presence of vanadium compounds, which are in this case more selective than molybdenum catalysts. The subsequent hydrolysis of glycidyl alcohol yields glycerine:



The dehydration of the alcohol formed from the hydroperoxide gives the corresponding olefin.

Some of these oxidative methods of glycerine synthesis have found industrial application, but because of the occurrence of many steps they have no decisive advantages over the chlorine method.

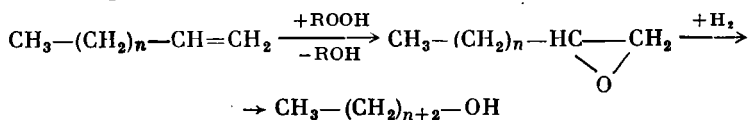
Synthesis of Isoprene. In the processes that have been described above, isopentane hydroperoxide may be used as the epoxidizing agent and the co-products formed are *tert*-amyl alcohol and isoamylene, the latter being converted to *isoprene* by an additional dehydrogenation; isoprene is a monomer for the manufacture of synthetic rubber. It is, however, possible to obtain only isoprene as the major product by carrying out the epoxidation of isoamylene, the isomerization or hydrolysis of its α -oxide and the dehydration of the resulting unsaturated alcohol or diol:



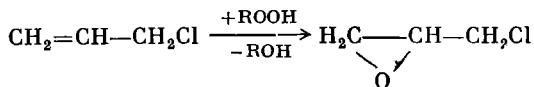
The last two steps (the isomerization of the α -oxide and the dehydration of the unsaturated alcohol) can be combined into a single step, since they proceed under similar conditions in the presence of the same heterogeneous catalyst.

The above oxidative method of preparation of isoprene is noted for a high yield of the major product (≈ 70 percent) and for the simplicity of its isolation and purification, which is why the method is likely to assume commercial importance.

The hydroperoxide epoxidation may be of practical value for the synthesis of primary alcohols from α -olefins:



for the synthesis of epichlorohydrin from allyl chloride:



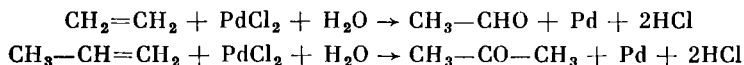
and for other combined processes.

6.4.2. Oxidation and Oxidative Coupling of Olefins Catalyzed by Metal Complexes

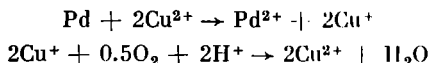
The first process developed and realized in industry in 1960 was the synthesis of acetaldehyde from ethylene; this synthesis can also be used for the production of other carbonyl compounds. Later the reactions of oxidative coupling of olefins assumed industrial importance, especially their acetoxylation involving the formation of vinyl acetate and other valuable compounds.

6.4.2.1. Synthesis of Carbonyl Compounds

The production of carbonyl compounds from olefins is based on the relatively long-known stoichiometric reaction of palladium chloride with olefins, in which PdCl_2 is reduced to the metal:



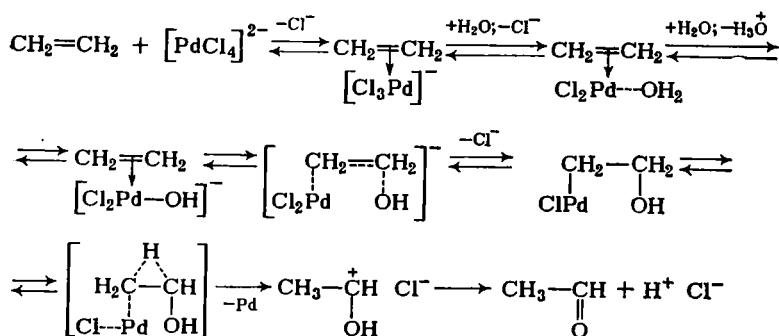
If oxygen is introduced together with the olefins into the reaction mass, palladium is oxidized, but the reaction proceeds very slowly. The commercial success of the process is due mainly to the oxidation-reduction (redox) system, in which palladium is rapidly oxidized, i.e., is continuously regenerated in active form. It has been found that if a cupric salt is added to the solution, it oxidizes palladium, being itself converted to a cuprous salt, which is readily oxidized by oxygen. In other words, copper salts serve here as oxygen carriers:



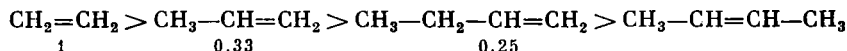
Both these reactions proceed effectively in an acidic medium, in which palladium chloride is in the form of H_2PdCl_4 .

The mechanism of the process involves the intermediate steps of substitution of chloride ions in the coordination sphere of the palladium complex by olefin and water molecules (this is responsible for the retarding effect of large concentrations of chloride ions). The coordination complex of palladium chloride with the olefin and water loses a proton reversibly, which explains why the reaction is slowed down at considerable concentrations of hydrogen ions.

The subsequent reaction proceeds inside the newly formed complex, with the hydroxyl ion attacking one of the unsaturated carbon atoms of the olefin with the simultaneous migration of the hydride ion to the neighbouring carbon atom and formation of metallic palladium. What has been said above about the oxidation of ethylene to acetaldehyde may be represented by the following scheme:



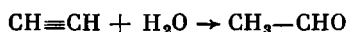
The reactivity of olefins in this reaction varies in the order characteristic of catalysis by means of metal complexes:



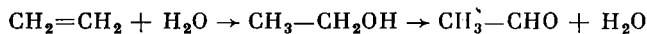
The oxidation occurs at the least hydrogenated carbon of the double bond, as a result of which acetaldehyde is formed only from ethylene and ketones are formed from the other olefins. Apart from ethylene homologues, cycloolefins and alkylaromatic compounds with a double bond in the side chain are also capable of undergoing this reaction.

As a result of the partial attack on the other unsaturated carbon-atom, a small amount of aldehydes is formed as by-products from α -olefins; for example, propionaldehyde is formed from propylene. Moreover, the chlorinating effect of copper chlorides results (especially upon oxidation of higher olefins) in the formation of by-product chloroketones, the amount of which increases with growing concentration of copper salts and with increasing acidity of the solution. The yield of the chloroketone upon oxidation of *n*-butylene may reach 10-30 percent, which is why measures must be taken either to reduce the yield of this by-product or to utilize it effectively.

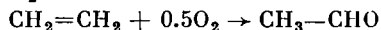
The synthesis described above has found industrial application chiefly for the production of *acetaldehyde*, whose properties and uses and methods of production from acetylene



have already been encountered (page 206). Acetaldehyde was also made by the hydration of ethylene to ethanol, which is then dehydrogenated to acetaldehyde:



The synthesis of acetaldehyde by the oxidation of ethylene over the catalyst $\text{PdCl}_2 \cdot \text{CuCl}_2$



gives a yield higher than 95 percent, this being unattainable by using other methods; it uses a cheaper raw material than acetylene and proceeds in a single step.

The economic indices of acetaldehyde production by the three principal methods are as follows:

Method	Product cost, percent	Capital cost, percent
Direct hydration of acetylene . . .	100	100
From ethylene via ethanol	85-95	60-70
Direct oxidation of ethylene	55-60	45-55

Thus, the method of acetaldehyde production by the direct oxidation of ethylene has distinct economical advantages over the other methods and it is replacing them in industry.

The same method can be used to obtain ketones (acetone, methyl ethyl ketone) from ethylene homologues, but their synthesis has not found wide application because of the availability of other, more economical processes (say, the production of acetone by the cumene method of phenol manufacture) and of the lower yield of ketones (85-90 percent) with the simultaneous formation of chloroketones, which are of little practical value.

Technology of Acetaldehyde Synthesis from Ethylene. In this process it is important to attain an appropriate relation between the rates of ethylene oxidation to PdCl_2 , oxidation of the reduced form of palladium with the aid of CuCl_2 and of the oxidation of Cu_2Cl_2 by oxygen. The last-named reaction is the slowest step, and the catalyst solution must therefore contain an excess of cuprous and cupric chlorides. For example, good results are obtained by using a weak hydrochloric-acid solution containing 0.3-0.5 percent of PdCl_2 and 10-25 percent of CuCl_2 , to which 2-3 percent of copper acetate is added to control the pH of the medium. With this solution all the steps occur at a sufficiently fast rate at 100-130 °C, but in order to maintain the liquid state of the reaction mixture there is required an elevated pressure (0.3-1 MPa), which also favours the intensification of the process.

The reaction units used for the process are bubble-cap columns, which are sometimes filled with a packing in order to intensify the mass transport from the gas to the liquid. One of the major problems encountered in the operation of this process was the choice of mate-

rials of construction for the reactor, where the highly acid metal chloride solutions were found to be very corrosive. A solution was found in the fabrication of critical items of equipment in titanium metal or other acid-resistant metals. The reactors used have no heat-exchangers and the reaction heat is removed by way of heating the cold reagents and of the evaporation. The process may be carried out either as a one-stage operation or as a two-stage operation.

In the two-stage process, the oxidation of ethylene by the catalyst solution and the regeneration of the catalyst solution by air are

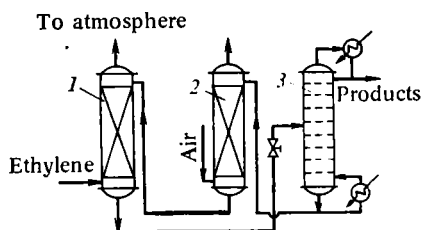


Fig. 6.31. Flow diagram of the two-stage synthesis of acetaldehyde by the air oxidation of ethylene:

1—reactor; 2—regenerator; 3—stripping column.

effected in two different vessels (Fig. 6.31). Ethylene and regenerated catalyst solution are fed into reactor 1 filled with an acid-resistant packing; the reaction is brought to a nearly complete conversion of ethylene at 0.8-0.9 MPa and 100-115 °C. The resultant acetaldehyde solution in the regenerated catalyst solution is throttled and transferred to stripping column 3, where the acetaldehyde and the dissolved gases are distilled off; the gases are then led for further

separation. The catalyst solution from the bottom of the stripper is pumped at ≈ 1 MPa to regeneration unit 2; air is also admitted into this unit to oxidize the salt to the highest valence state. The regenerated solution is then returned to reactor 1. The advantages of the two-stage process are the safety of the operation (the stages involving ethylene and air are carried out separately) and the use of air as the oxidizing agent.

In the one-stage method, the oxidation of ethylene and the regeneration of the catalyst are carried out jointly in a single reactor. In order to prevent the formation of explosive mixtures, the process is carried out in an excess of ethylene, which is then returned to the reaction. This requires the use of technical oxygen (and not air) as the oxidizing agent; the conversion of oxygen in the reactor must be almost complete.

The flow diagram of the one-stage process is given in Fig. 6.32. Oxygen and ethylene (fresh and recycle ethylene) are fed into reactor 1 (a hollow bubble-cap column) filled with the catalyst solution. The reactor operates at a constant liquid level at 130 °C and ≈ 0.3 MPa. The excess ethylene purges the acetaldehyde from the solution, thereby preventing the side reactions of its condensation. Part of the water is evaporated together with the acetaldehyde, condensed in cooler 3 and returned to the reactor.

The gas-steam mixture is led to absorber 4, where the acetaldehyde is absorbed by the water that refluxes the packing of the absorber. The major proportion of the residual gas containing ethylene, a small amount of oxygen and inert impurities is additionally compressed by circulation compressor 2 and recycled to the oxidation. The remaining portion of the gas is withdrawn from the plant in order to avoid the excessive accumulation of the inert impurities. The aqueous solution of acetaldehyde passes from the still of absorber 4 to stripping column 5, where the dissolved gases and volatile impurities are distilled off. Acetaldehyde is recovered as the distillate in

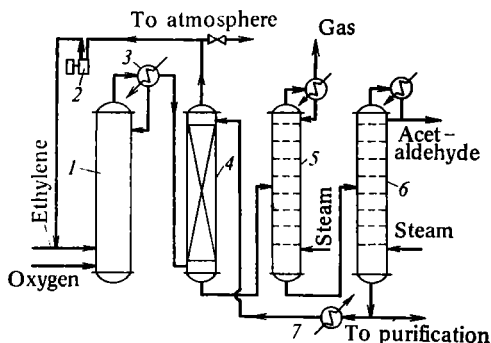


Fig. 6.32. Flow diagram of the one-stage synthesis of acetaldehyde by the oxidation of ethylene by oxygen:

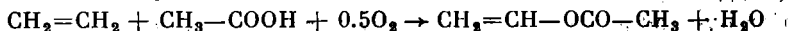
1—reactor; 2—circulation compressor; 3—cooler; 4—absorber; 5—stripper; 6—fractionating column; 7—cooler.

column 6 and the major proportion of the still liquid, which contains less volatile by-products (crotonaldehyde, etc.), is cooled and returned to absorption. Part of this liquid is transferred to the waste water purification system.

As compared with the two-stage process, in the one-stage synthesis of acetaldehyde the capital cost and the power consumption are lower, but it uses a more expensive oxidizing agent (oxygen). These methods are, in general, similar in economical indices and are successfully used in industry.

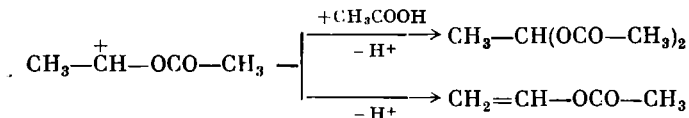
6.4.2.2. Processes of Oxidative Coupling

Synthesis of Vinyl Acetate from Ethylene. The properties, uses and methods of production of vinyl acetate have been described earlier (page 314). Because of the use of expensive acetylene, this method is replaced by another method based on the oxidative coupling of ethylene with acetic acid:



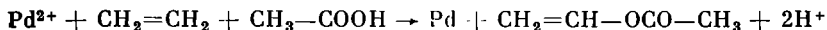
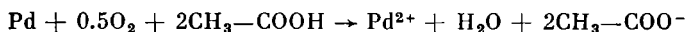
This reaction was discovered about 20 years ago by the Soviet chemist I. I. Moiseev. Like the synthesis of acetaldehyde, this reaction is effected in the presence of catalysts based on palladium. If their interaction occurs not in an aqueous solution but in the medium of glacial acetic acid, then the carbonium ion has the structure

$\text{CH}_3-\overset{+}{\text{CH}}-\text{OCO}-\text{CH}_3$ and can react not only with a second acetic acid molecule, forming ethylidene diacetate but it can also split off a proton with the formation of vinyl acetate:



Such a *liquid-phase* process was conducted over the catalyst $\text{PdCl}_2 \times \text{CuCl}_2$ in the medium of acetic acid with sodium acetate or lithium chloride added. Apart from ethylidene diacetate, the by-products formed are *n*-butylene (due to the dimerization of ethylene) and acetaldehyde. Since the production of vinyl acetate involves the formation of water, the accumulation of the latter in the reaction medium results in an increase in the yield of acetaldehyde. With a definite ratio of acetic acid to water kept constant it is possible to combine the synthesis of vinyl acetate and that of acetaldehyde as a single process. Because of the relatively low yield of the products and the corrosive effects, the liquid-phase process has been superseded by the gas-phase operation, which has been universally adopted.

The *gas-phase* synthesis of vinyl acetate is carried out over a heterogeneous catalyst (Pd on SiO_2 , Al_2O_3 or on aluminosilicate with sodium acetate added), in which the role of copper salts is played by the support, which favours the oxidation of palladium to the divalent form:



The reaction conditions are 170-180 °C and 0.5-1 MPa. The gas-steam mixture of the reactants is passed through the heterogeneous catalyst. In order to avoid the formation of explosive mixtures, ethylene and acetic acid are taken in excess. The unconverted ethylene is returned to oxidation, which requires the use of oxygen (and not air) as the oxidizing agent. The feed mixture consists of ethylene, acetic acid vapours and oxygen in a volume ratio of $\approx 8:4:1$. The degree of conversion of the components of the mixture per pass through the reactor is 10, 20, and 60-70 percent, respectively. The selectivity with respect to vinyl acetate reaches 91-92 percent; the major by-product is CO_2 and only 1 percent of other compounds is formed (ethyl acetate, ethylidene diacetate).

The flow diagram of the synthesis of vinyl acetate in the gas phase is shown in Fig. 6.33. A mixture of fresh and recycle ethylene and acetic acid is heated in steam heater 1, mixed with fresh oxygen and led to tubular contact vessel 2 containing a fixed catalyst bed in the tubes. The heat evolved is removed by way of the evaporation (in the intertubular space) of the water condensate; this produces steam, which is separated in collector 3. The reaction mixture is cooled in cooler 4 and the gas is washed successively in scrubbers 5 and 6 by the recycle acetic acid and water to recover vinyl acetate

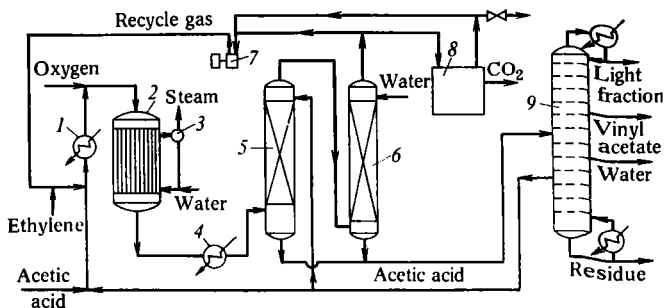


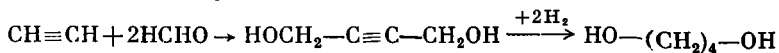
Fig. 6.33. Flow diagram of the synthesis of vinyl acetate from ethylene:

1—steam heater; 2—reactor; 3—steam collector; 4—cooler; 5, 6—scrubbers; 7—circulation compressor; 8—unit for carbonate purification from CO_2 ; 9—system of fractionating columns.

and acetic acid, respectively. The greater part of the washed gas is returned by circulation compressor 7 to synthesis, but part of it passes through unit 8 to be subjected to carbonate purification from CO_2 ; unit 8 is similar to that shown in Fig. 6.29. The major proportion of the purified gas is recycled, but some portion of it is withdrawn from the system in order to avoid excessive accumulation of the inert impurities contained in ethylene and oxygen. The mixture of liquid products from the still of scrubbers 5 and 6 is led for separation to a system of fractionating columns 9, where the vinyl acetate, water, acetic acid and heavy impurities are separated; the impurities are burned.

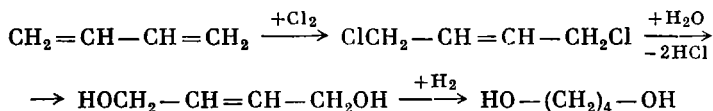
Synthesis of 1,4-Butanediol. This product is very valuable because it is used for the production of plasticizers (the esters of $\text{C}_7\text{--C}_9$ carboxylic acids), polyesters and tetrahydrofuran.

The first method of its synthesis (the Reppe synthesis) from acetylene and formaldehyde



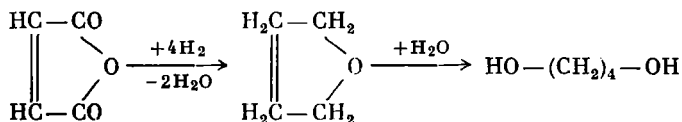
lost its practical importance because of the use of expensive acetylene and of the complexity of the apparatus used.

Another method involves the incomplete chlorination of butadiene (page 126) with the formation of 1,4 and 1,2-dichlorobutenes. When subjected to hydrolysis and subsequent hydrogenation the first isomer gives 1,4-butanediol:

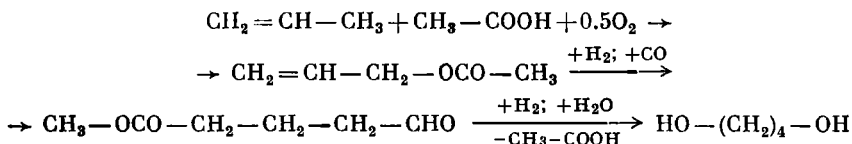


This method involves the consumption of chlorine and is likely to be in less favour.

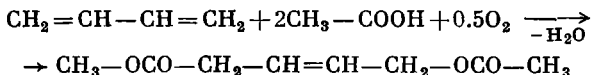
A further possibility is to hydrogenate maleic anhydride to tetrahydrofuran with the subsequent hydrolysis of tetrahydrofuran to the diol:



A promising method today is the acetoxylation of propylene over a palladium catalyst. Under conditions similar to those used for the synthesis of vinyl acetate propylene gives allyl acetate, which undergoes hydroformylation, hydrogenation and hydrolysis to form 1,4-butanediol:

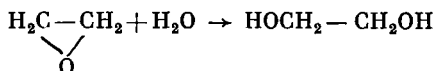


It is simpler to obtain butanediol from 1,3-butadiene, which upon acetoxylation gives mainly 1,4-butanediol diacetate:



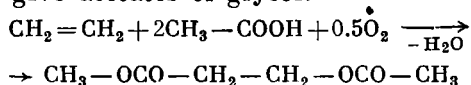
The by-product formed is the 1,2-isomer, which can be converted to the 1,4-isomer by the action of acid catalysts. The hydrolysis and hydrogenation of this isomer lead to 1,4-butanediol and acetic acid, the latter being recycled to the reaction. The yield of the products reaches 85 percent on butadiene.

A New Synthesis of Ethylene Glycol. In the conventional method of production of ethylene glycol via ethylene oxide (page 303)



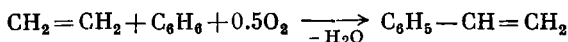
the yield of the glycol is relatively low because of the insufficiently high selectivity of ethylene oxidation (it is only 70 percent).

A new method of synthesis involves two steps. First, ethylene is acetoxylation to give acetates of glycol:

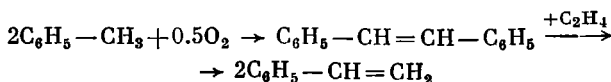


The product obtained consists of 60 percent of the diacetate, 35 percent of the monoacetate and 5 percent of ethylene glycol, the overall selectivity of their formation being 97 percent. The catalysts used are a mixture of palladium and copper chlorides, palladium nitrate and especially TeO_2 promoted with bromine compounds. The synthesis is effected at 160 °C and ≈ 2.8 MPa with a 60-percent conversion of ethylene and with circulation of the unconverted gases. The second step is the hydrolysis of the resultant mixture by water at 110–130 °C, in which acetic acid (to be recycled) and ethylene glycol are produced. The total yield of ethylene glycol reaches 94 percent on ethylene, which considerably exceeds the yield of the conventional method of synthesis. Large plants designed for the production of ethylene glycol are reported to be operating according to this method, but no reliable data on the technology and economy of the production are available.

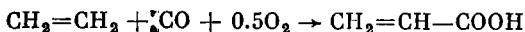
The above-described reactions of oxidative coupling have been used as the prototype for the development of some other processes: the synthesis of styrene from ethylene and benzene:



or from toluene via stilbene:



the manufacture of acrylic acid from ethylene



and a number of other reactions, which may find practical application, all this being evidence of the increasing importance of metal-complex catalysis in the oxidative conversions of hydrocarbons.

DEHYDROGENATION AND HYDROGENATION PROCESSES

Dehydrogenation embraces chemical processes involving the removal of hydrogen atoms from organic compounds. *Hydrogenation* (or *hydrogenolysis*) may be defined as the reaction of organic compounds with molecular hydrogen. In a number of cases, hydrogenation results in the reduction of oxygen-containing compounds and dehydrogenation leads to their oxidation.

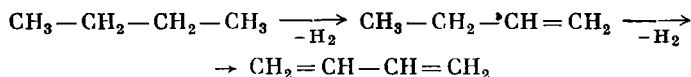
Dehydrogenation and hydrogenation processes are very important in the industry of organic synthesis. The dehydrogenation reaction is used to produce unsaturated compounds that are of great value as monomers for the production of synthetic rubber and plastics (1,3-butadiene, isoprene, styrene) and also of some aldehydes and ketones (formaldehyde, acetone, methyl ethyl ketone). The hydrogenation reactions are employed to synthesize cyclohexane and its derivatives, many amines (aniline, hexamethylenediamine), alcohols (*n*-propyl, *n*-butyl and higher alcohols). Hydrogenation processes are also used for the hydrogenation of fats and oils and for the production of liquid fuels (hydrocracking, reforming, hydrogenolysis of coal, etc.). Hydrogenation and dehydrogenation reactions are very often the steps of multistep syntheses of valuable organic compounds—monomers, surface-active agents (surfactants), solvents, etc.

The scale of production of some dehydrogenation and hydrogenation products can be estimated on the basis of the following data on their production in the USA (the forecast for 1980, in million tons):

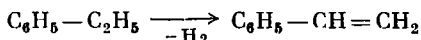
Styrene	4.0
Formaldehyde (100-percent)	3.4
1,3-Butadiene	2.5
Cyclohexane	1.3
Hexamethylenediamine	0.35
Aniline	0.3
Isoprene	0.25

Classification of Dehydrogenation Reactions. The most typical dehydrogenation reactions may be classified according to the type of the bond between the atoms from which a hydrogen is split off (C—C, C—O and C—N dehydrogenations).

The C—C dehydrogenation of paraffins gives compounds with a double carbon-carbon bond; the further progress of the reaction results in the formation of dienes:



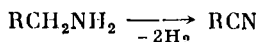
The side chains of aromatic compounds can also be dehydrogenated with the formation of compounds of the styrene type:



The dehydrogenation at the C—O bond is typical of primary and secondary alcohols, from which aldehydes and ketones are formed, respectively:

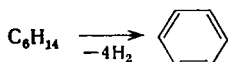


An example of dehydrogenation at the C—N bond is the removal of hydrogen from primary amines, which leads to the formation of nitriles:



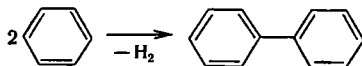
In all the reactions described above the initial arrangement of atoms in the chain is retained, but there are dehydrogenation processes that proceed with a change in the atomic arrangement.

Of importance is the *dehydrocyclization* process, in which paraffinic hydrocarbons undergo a ring closure and dehydrogenation to give aromatic hydrocarbons:



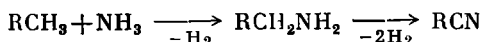
This is the most important route to the aromatization of the narrow fractions of petroleum; it has already been described (see Chapter 1).

Another type of dehydrogenation reactions, *dehydrocondensation*, leads to di- and polycyclic compounds:

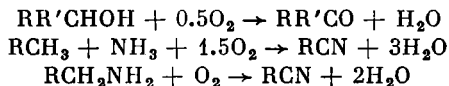


and eventually to the formation of highly condensed-ring hydrocarbons. The occurrence of dehydrocondensation accounts for the formation of coke in the pyrolysis of petroleum products and natural gas.

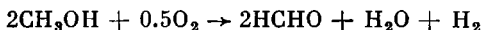
A different type of dehydrocondensation is observed in the synthesis of amines and nitriles from hydrocarbons and ammonia, in which new C—N bonds are formed:



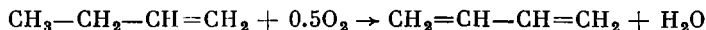
Many of the conversions described above can be carried out with the aid of oxidation reactions; some examples are the synthesis of carbonyl compounds from alcohols, the synthesis of nitriles from hydrocarbons and ammonia, the synthesis of nitriles from amines:



Such reactions can sometimes be effected at an oxygen deficiency and involve the simultaneous oxidation and dehydrogenation:



In other cases, the amount of oxygen taken is greater than that required by the stoichiometry, but the reaction is reduced to dehydrogenation:

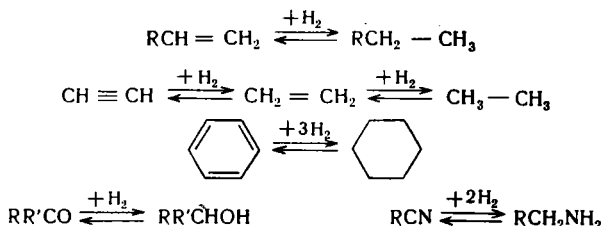


Processes of this type are called *oxidative dehydrogenations*. They are intermediate between oxidation and dehydrogenation; in some cases, they are so close to oxidation that it becomes difficult to draw a distinct boundary line between oxidation and oxidative dehydrogenation.

Classification of Hydrogenation Reactions. Hydrogenation reactions may be divided into three groups:

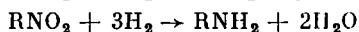
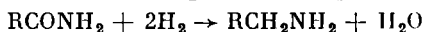
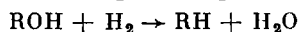
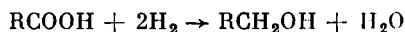
- (1) addition of hydrogen to unsaturated bonds;
- (2) the action of hydrogen accompanied by the liberation of water or other substances that do not contain carbon;
- (3) reactions with hydrogen accompanied by the cleavage of carbon-carbon bonds (destructive hydrogenation or hydrogenolysis).

The reactions of the first group are the reverse of the above-described dehydrogenation with retention of the initial arrangement of atoms in the chain. They can occur with addition of hydrogen to double, triple and aromatic carbon-carbon bonds, the C—O bonds of aldehydes and ketones, the C=N and C≡N bonds of nitrogen compounds, etc.:

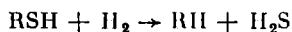


The reactions written above clearly demonstrate the hydrogenation-dehydrogenation reversibility, which is an essential feature of these processes.

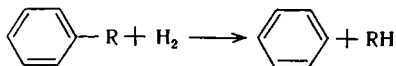
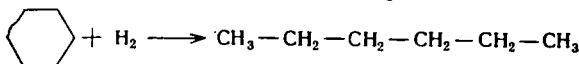
The second group of hydrogenation reactions corresponds to the reduction of organic compounds (though the reduction also includes the conversion of carbonyl compounds to alcohols, which is not accompanied by the liberation of water). The second-group processes include the hydrogenation of carbonyl acids to alcohols, of alcohols to hydrocarbons, of acid amides and nitro compounds to amines, etc.:



In these reactions, not only water but also hydrogen chloride, ammonia, hydrogen sulphide, etc., can be eliminated:

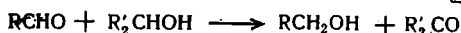


The third group of hydrogenation reactions, which involve the cleavage of carbon-carbon bonds, is called *destructive hydrogenation* or *hydrogenolysis* (by analogy with hydrolysis, alcoholysis, etc.). The tendency to undergo hydrogenolysis is exhibited by open-chain hydrocarbons, naphthenes, aromatic compounds with a side chain:



These reactions are thus the reverse of the dehydrocondensation and dehydrocyclization processes. Not infrequently, the above-mentioned hydrogenation reactions involving the liberation of water and especially of H_2S and NH_3 , when the molecule is cleaved across the C—S or C—N bonds, are also classified as destructive hydrogenation processes.

A special type of hydrogenation-dehydrogenation reactions is the *hydrogen redistribution* between two molecules, when one of them loses hydrogen and the other adds it (the dehydrohydrogenation reaction). Often, in such cases no hydrogen molecule is required at all. Such processes are important in the processing of petroleum products (reforming, etc.) and are used in organic synthesis:



7.1. Physico-Chemical Foundations of Dehydrogenation and Hydrogenation Processes

Dehydrogenation and hydrogenation reactions have many common features in their physico-chemical regularities, since they constitute a system of reversible transformations. Their thermodynamics, kinetics, catalysis and also the problems of the choice of optimum conditions can conveniently be described by comparing dehydrogenation and hydrogenation processes.

7.1.1. Thermodynamics of Dehydrogenation and Hydrogenation Reactions

Thermochemical Data. Below are given the heat effects of principal hydrogenation reactions for the gaseous state of all substances. It is obvious that for dehydrogenation processes, which are the reverse of the corresponding hydrogenation reactions, the heat effects have the same absolute value but are opposite in sign:

Reaction	$-\Delta H_{298}^{\circ}$	
	kJ/mol	kcal/mol
(1) $\text{RCH}=\text{CH}_2 \xrightarrow{+\text{H}_2} \text{RCH}_2-\text{CH}_3$	113-134	27-32
(2) $\text{CH}\equiv\text{CH} \xrightarrow{+2\text{H}_2} \text{CH}_3-\text{CH}_3$	311	74.4
(3) $\text{C}_6\text{H}_6 \xrightarrow{+3\text{H}_2} \text{C}_6\text{H}_{12}$	206	49.3
(4) $\text{RCHO} \xrightarrow{+\text{H}_2\text{O}} \text{RCH}_2\text{OH}$	67-83	16-20
(5) $\text{R}_2\text{CO} \xrightarrow{+\text{H}_2} \text{R}_2\text{CHOH}$	≈ 58	≈ 14
(6) $\text{RCN} \xrightarrow{+2\text{H}_2} \text{RCH}_2\text{NH}_2$	134-159	32-38
(7) $\text{RCOOH} \xrightarrow[+\text{H}_2\text{O}]{2\text{H}_2} \text{RCH}_2\text{OH}$	38-42	9-10
(8) $\text{RNO}_2 \xrightarrow[-2\text{H}_2\text{O}]{+3\text{H}_2} \text{RNH}_2$	439-472	105-113
(9) $-\text{CH}_2-\text{CH}_2- \xrightarrow{+\text{H}_2} -\text{CH}_3 + -\text{CH}_3$	42-63	10-15

From the data given it can be seen that all hydrogenation reactions are exothermic and dehydrogenation reactions always proceed with the absorption of heat.

When calculated per one hydrogen molecule added the heat effect proves to be the highest for compounds with a triple carbon-carbon bond. For aromatic systems it is lower than for olefins, which is accounted for by the disturbance of the stable system of aromatic bonds. The heat effect of the hydrogenation of carbonyl groups is

lower than in the case of a double carbon-carbon bond. The hydrogenation of aldehydes (reaction 4) is more exothermic than the hydrogenation of ketones (reaction 5). A similar heat effect per hydrogen molecule added is displayed by the hydrogenation of nitriles (reaction 6). Obviously, the same regularities referred to the absorption of heat are observed for reverse dehydrogenation reactions. Of the two hydrogenation reactions involving the liberation of water (reactions

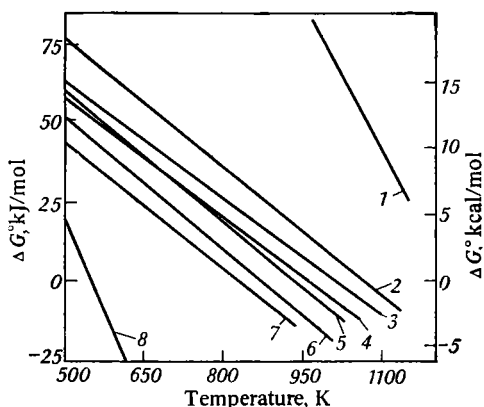


Fig. 7.1. Temperature dependence of the free-energy change of the dehydrogenation of hydrocarbons:

- (1) $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_2 + 2\text{H}_2$; (2) $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$;
- (3) $n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{C}_4\text{H}_8 + \text{H}_2$; (4) $\text{C}_6\text{H}_5\text{—C}_2\text{H}_5 \rightleftharpoons \text{C}_6\text{H}_5\text{—CH=CH}_2 + \text{H}_2$; (5) $n\text{-C}_4\text{H}_{10} \rightleftharpoons n\text{-C}_4\text{H}_8 + \text{H}_2$;
- (6) $\text{iso-C}_4\text{H}_{10} \rightleftharpoons \text{iso-C}_4\text{H}_8 + \text{H}_2$; (7) $\text{C}_6\text{H}_5\text{—CH(CH}_3)_2 \rightleftharpoons \text{C}_6\text{H}_5\text{—C(CH}_3)=\text{CH}_2 + \text{H}_2$;
- (8) $\text{C}_6\text{H}_{12} \rightleftharpoons \text{C}_6\text{H}_6 + 3\text{H}_2$.

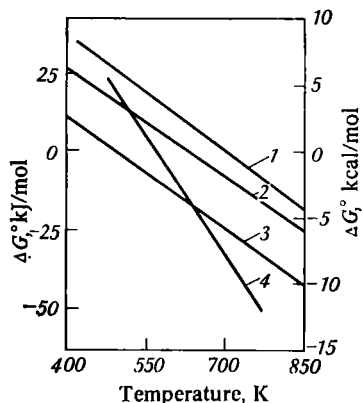


Fig. 7.2. Temperature dependence of the free-energy change for the dehydrogenation of alcohols and amines:

- (1) $\text{CH}_3\text{OH} \rightleftharpoons \text{HCHO} + \text{H}_2$;
- (2) $\text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2$;
- (3) $\text{CH}_3\text{CH(OH)CH}_3 \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{H}_2$;
- (4) $\text{C}_2\text{H}_5\text{NH}_2 \rightleftharpoons \text{CH}_3\text{CN} + 2\text{H}_2$.

7 and 8), one has the lowest heat effect and the second, the highest heat effect among all the hydrogenation processes given above. Destructive hydrogenation at a carbon-carbon bond (reaction 9) is accompanied by the evolution of a relatively small amount of heat.

The exothermicity of hydrogenation reactions and the endothermicity of dehydrogenation reactions have a strong impact on the technology of these processes.

The heat effect of oxidative dehydrogenations depends on the fraction of oxidation reactions and dehydrogenation proper. Since oxidation reactions always proceed with the evolution of heat, the heat effect of the overall conversion can be varied within wide limits by introducing various amounts of oxygen. This is one of the advantages of oxidative dehydrogenation—the endothermicity of the process is eliminated and the reaction system need not be constantly heated.

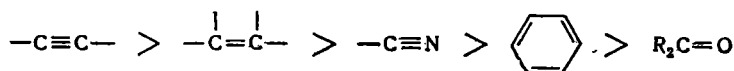
The Equilibrium of Hydrogenation and Dehydrogenation Reactions. A very important feature of the majority of hydrogenation reactions and of all dehydrogenation processes is their reversibility. Obviously, because of the exothermicity of hydrogenation, the equilibrium will be shifted to its side at low temperatures, and for endothermic dehydrogenation reactions, on the contrary, a high temperature is favourable. The temperature dependences of the free energy change for the most interesting dehydrogenation processes are given graphically in Figs 7.1 and 7.2. For hydrogenations they have the same absolute value but are opposite in sign. The near-zero or positive values of ΔG° point to the feasibility of the reaction and to the shift of the equilibrium in accordance with the well-known equation:

$$\Delta G^\circ = -RT \ln K_p$$

From Fig. 7.1 it follows that with increasing molecular mass of the paraffin (straight lines 2 and 5) the equilibrium becomes more favourable for dehydrogenation. The presence of phenyl substituents and the branching of the carbon chain favour the elimination of hydrogen (straight lines 4, 6 and 7). The dehydrogenation of six-membered naphthenes occurs most readily (straight line 8), which is accounted for by the formation of a stable aromatic system. Conversely, the removal of hydrogen with the formation of hydrocarbons having conjugated double bonds (straight line 3) and especially of those having triple bonds (straight line 1) is thermodynamically the least favourable.

Figure 7.2 shows that for alcohols and amines the thermodynamic relationships upon dehydrogenation are more favourable than for any hydrocarbon, except for six-membered naphthenes. The equilibrium is displaced more strongly to the right in secondary alcohols (in the formation of ketones) and in primary amines (in the formation of nitriles) and less strongly for primary alcohols (especially for methanol), which give aldehydes upon dehydrogenation.

The thermodynamic relationships for hydrogenation are reversed. Here the equilibrium is more favourable for the hydrogenation of lower olefins, dienes and especially acetylenic hydrocarbons, the presence of phenyl substituents and branched carbon chains having a negative effect. The conditions for the hydrogenation of aldehydes, nitriles, ketones and aromatic rings are less favourable. If we compare the reactivities with respect to hydrogenation for the temperature at which $K = 1$ and $\Delta G^\circ = 0$ (with only thermodynamic factors being taken into account), we will obtain the following order:



For dehydrogenation leading to the formation of the same functional groups or bonds the order is reversed; it may somewhat change if other conditions are chosen for comparison.

In hydrogenation processes accompanied by the liberation of water, the equilibrium is typically shifted to the right more strongly than in the cases just considered. For example, the hydrogenation of alcohols to hydrocarbons and of nitro compounds to amines is practically irreversible at all permissible temperatures. An exception is the conversion of carboxylic acids to alcohols:



which is accompanied by a slight change in the free energy under standard conditions (it is equal to $\Delta G^\circ = -21.3$ kJ/mol or -5.1 kcal/mol); the equilibrium constant decreases with increasing temperature.

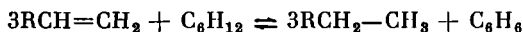
The thermodynamic relationships considered above can easily be applied to reactions of the catalytic hydrogen redistribution. If the equilibrium constants K_1 and K_2 are equal for the hydrogenation of two compounds at a given temperature:



then, dividing them by each other, we obtain the equilibrium constant K_p for the hydrogen redistribution reaction:

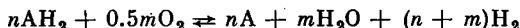


The equilibrium of the hydrogen redistribution reaction will be shifted to the right if $K_1 > K_2$, i.e., when substance A is thermodynamically more liable to hydrogenation as compared with substance B. This explains why in the systems



the equilibrium is considerably displaced to the right.

The peculiarities of oxidative dehydrogenation are due to the fact that during its occurrence, part of hydrogen is combined into water, which does not participate in the equilibrium of hydrogenation-dehydrogenation reactions:



The equilibrium of such processes therefore depends on the oxidation-dehydrogenation ratio. With other conditions being equal, it is always shifted more strongly to the right than in the case of dehydro-

genation proper, and this is one of the advantages of oxidative dehydrogenation.

Effect of Thermodynamic Factors on the Choice of Reaction Conditions. In order to attain a sufficiently high degree of conversion for reversible hydrogenation-dehydrogenation processes, it is necessary to choose such conditions under which the most favourable equilibrium position is provided, which depends on the thermodynamic factors.

It is clear from the considerations given above that *dehydrogenation* processes must be carried out at a relatively high temperature, which varies from 200 to 600-650 °C, depending on the technological process. It depends on the type of the feedstock and is chiefly determined by the specific thermodynamic features of the reaction. For example, the dehydrogenation of alcohols and amines, which are more liable to this reaction, is effected at 200-400 °C, whereas the production of olefins, dienes and arylolefins requires a temperature of 500-650 °C. From this it follows that all dehydrogenation processes must be carried out in the gas phase. Because of the elimination of hydrogen, dehydrogenation always involves an increase in the gas volume and, hence, the increase of the degree of conversion is favoured by a low pressure. For this reason, the pressure chosen for dehydrogenation processes is close to atmospheric, and in some cases the process is conducted in vacuum. For instance, at 595 °C the equilibrium degree of conversion of ethylbenzene to styrene at ≈ 0.1 MPa is 40 percent, and at ≈ 0.01 MPa it sharply increases to 80 percent. A typical curve illustrating the effect of pressure is given in Fig. 7.3 for the dehydrogenation of *n*-butylene to butadiene. When more than one hydrogen molecule is eliminated, the dependence shown is even more sharply pronounced.

Instead of using a vacuum, it is sometimes convenient to dilute the reaction mass by a gas or steam (which is inert under the reaction conditions), which also leads to a decrease in the partial pressures of the reactants and to an increase in the equilibrium degree of conversion. Since hydrogen shifts the equilibrium to the side of hydrogenation and other gases complicate the recovery of valuable products, use is often made in practice of superheated steam with the total pressure of ≈ 0.1 MPa being kept constant. The effect of steam dilution on the degree of equilibrium conversion is similar to that shown in Fig. 7.3.

From thermodynamic considerations, *hydrogenation* processes should be carried out at as low a temperature as possible, which, however, makes it possible to attain the suitable reaction rate. In industrial practice, the temperature varies from 100 to 350-400 °C (depending on the activity of the catalyst and the reactivity of the starting material). In the region of relatively low temperatures the equilibrium (as can be seen from Figs. 7.1 and 7.2) is shifted almost

completely to the side of hydrogenation, which is why the reaction may be carried out almost entirely at atmospheric pressure. Since the hydrogenation always involves a decrease in volume (because of the hydrogen being absorbed), for the equilibrium degree of conversion to the increased use is very often (especially at relatively high temperatures) made of elevated pressure. In such conditions, which are far from ideal, the equilibrium constant depends on the

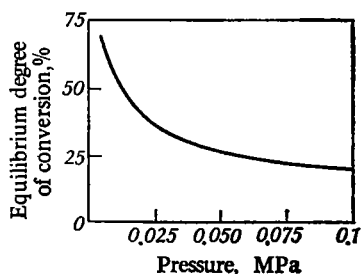


Fig. 7.3. Dependence of the equilibrium degree of conversion of *n*-butylene on the total pressure of the reagents for the dehydrogenation of *n*-butylene to butadiene at 860 K.

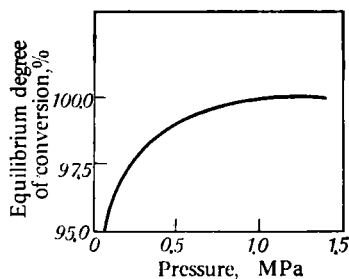
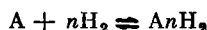


Fig. 7.4. Dependence of the equilibrium degree of conversion of benzene on the total pressure of the reagents for the hydrogenation of benzene to cyclohexane at 200 °C and a C_6H_6/H_2 ratio of 1 : 3.

molar fractions N of the reactants and their fugacity γ . For instance, for reactions in which n moles of hydrogen are added



the following equation for the equilibrium constant is valid:

$$K_p = \frac{P_{AnH_2}}{P_A P_{H_2}^n} = \frac{1}{P^n} \cdot \frac{N_{AnH_2}}{N_A N_{H_2}^n} \cdot \frac{\gamma_{AnH_2}}{\gamma_A \gamma_{H_2}^n} = \frac{1}{P^n} K_N K_\gamma$$

The molar fraction of the hydrogenation product increases with increasing pressure, the increase being the greater the larger is the number of hydrogen molecules added according to the stoichiometric equation of the reaction. Since the equilibrium degree of conversion figures both in the numerator and in the denominator of the expression for K_N , the dependence of the degree of conversion on pressure is usually expressed by a saturation curve (Fig. 7.4), which is typical of all hydrogenation processes. The pressure employed in industrial practice ranges from 1.5-5 to 30-40 MPa.

Another means of increasing the equilibrium degree of conversion is to use an excess of hydrogen as compared with the stoichiometric amount, this being widely practised for the gas-phase hydrogenation. For example, the hydrogenation of benzene at ≈ 0.1 MPa, 200 °C

and a molar ratio of $C_6H_6:H_2 = 1:3$ provides a 95.7-percent conversion, which increases to 99.5 percent with a tenfold excess of hydrogen.

7.1.2. Catalysis, Mechanism and Kinetics of Dehydrogenation and Hydrogenation Reactions

All hydrogenation and dehydrogenation reactions are catalytic, except thermal conversions, which occur at a high temperature and are accompanied by a strong decomposition and condensation. The use of catalysts makes it possible to attain a high reaction velocity at a relatively low temperature, when the undesirable side reactions have not yet developed to a considerable extent. Because of the reversibility of dehydrogenation-hydrogenation reactions and of the ability of any catalyst to accelerate both the forward and the reverse process, both reactions can, in principle, be catalyzed by the same substances. The catalysts used may be divided into three main groups:

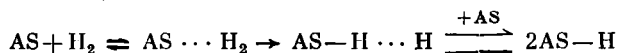
(1) the metals of Group VIII (Fe, Co, Ni, Pd, Pt) and those of Subgroup IB (Cu, Ag) of the Periodic System and also mixtures of these metals (alloys);

(2) metal oxides (MgO , ZnO , Cr_2O_3 , Fe_2O_3 , etc.);

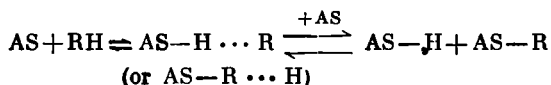
(3) complex oxide and sulphide catalysts composed of a mixture or compounds of oxides or sulphides (chromites— $CuO \cdot Cr_2O_3$ and $ZnO \cdot Cr_2O_3$, molybdates and tungstates— $CoO \cdot MoO_3$, $NiO \cdot WO_3$, $CoO \cdot WO_3$).

These substances, especially metals, are often supported on porous carriers and various promoters are added, such as the oxides of other metals, alkalis, etc. The catalysts are used in various forms, ranging from those finely dispersed to moulded porous forms (cylinders, rings, pellets). Their activity and selectivity vary, depending on the process; no general criteria have yet been established for the optimal choice of catalysts.

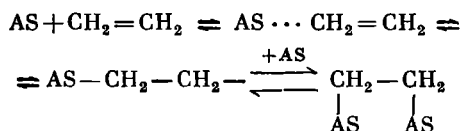
Mechanism of Hydrogenation and Dehydrogenation Reactions. These processes belong to the category of homolytic transformations, which are, in principle, similar to heterogeneous-catalytic oxidation reactions. An important role is played by the chemisorption of the reactants on the active regions or sites of the catalyst (AS), in which the chemical bonds in the adsorbed molecule are weakened or completely ruptured as a result of electron transfers with the participation of the catalyst. The application of various methods has demonstrated that when hydrogen is sorbed by metals, the physical adsorption is followed by a partial weakening of the bonds and the dissociation of the molecule (AS stands for the active site of the catalyst):



Saturated hydrocarbons are sorbed to a lesser extent, but the dissociation at the C—H bond is also possible for them:

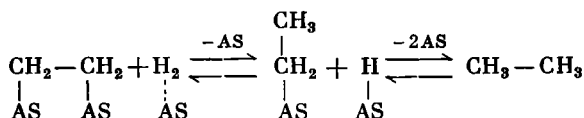


Olefins, aromatic compounds and notably acetylene and its homologues display a strong tendency towards sorption, which occurs due mainly to a partial or complete opening of the unsaturated bond:

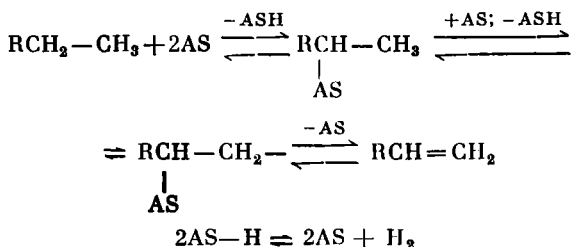


Oxide catalysts behave in a similar manner, but their ability to chemisorb hydrogen and hydrocarbons is weaker than that of metals. Organic oxygen-containing and nitrogen compounds are sorbed better on oxide catalysts than on metals.

The subsequent interaction occurs between the two chemisorbed particles residing on the neighbouring active sites of the surface or between the chemisorbed particle and a physically adsorbed molecule or a molecule ejected from the bulk. Here, in equilibrium hydrogenation-dehydrogenation processes each of the elementary steps is reversible:

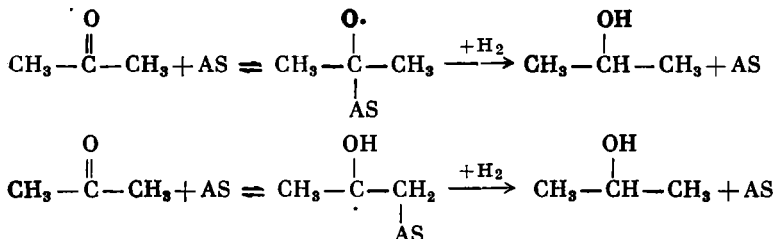


or



The hydrogenation of carbonyl compounds and the dehydrogenation of alcohols have some specific features. They may occur by the carbonyl mechanism with the chemisorption at the C—O bond and also by the enol mechanism, in which the reaction occurs across the C—C bond and involves the step of enolization of the carbonyl compound. Experiments involving labeled compounds have shown that the first mechanism predominates at a low temperature and

the second at a higher temperature:



Kinetics of Hydrogenation and Dehydrogenation Reactions. The rates of these reactions, just as those of other heterogeneous-catalytic processes, may depend, in a general case, on the diffusion and kinetic factors. The role of the diffusion factors is the less significant, the more intensive the stirring and turbulence of the streams and the lower the temperature. In most cases, the kinetics of hydrogenation and dehydrogenation is described by the general Langmuir-Hinshelwood equation, which has been derived for a case where the rate-limiting step is the chemical reaction taking place on the catalyst surface. If we denote the adsorption coefficients by b and the partial pressures of the reactants by P , then for a reversible dehydrogenation reaction with a unimolecular elimination of the sorbed compound we have:

$$r = k' \frac{P_{\text{AH}_2} - \frac{P_{\text{A}}P_{\text{H}_2}}{K_p}}{1 + b_{\text{AH}_2}P_{\text{AH}_2} + b_{\text{A}}P_{\text{A}} + b_{\text{H}_2}P_{\text{H}_2}}$$

and for the interaction of the chemisorbed compound with the other active sites of the surface we obtain

$$r' = k' \frac{P_{\text{AH}_2} - \frac{P_{\text{A}}P_{\text{H}_2}}{K_p}}{(1 + b_{\text{AH}_2}P_{\text{AH}_2} + b_{\text{A}}P_{\text{A}} + b_{\text{H}_2}P_{\text{H}_2})^2}$$

Depending on the value of the adsorption coefficients, these equations are often simplified. It is essential that the chemisorption of the dehydrogenated product A is normally much stronger than that of the saturated compound AH_2 and hydrogen, and that not only the unity in the denominator of the equations may be neglected but the other terms as well, with the exception of $b_{\text{A}}P_{\text{A}}$. For example, for the rate of the dehydrogenation of *n*-butane to *n*-butylene the following equation has been experimentally found:

$$r = k \frac{P_{\text{C}_4\text{H}_{10}} - \frac{P_{\text{C}_2\text{H}_4}P_{\text{H}_2}}{K_p}}{P_{\text{C}_4\text{H}_8}}$$

which points to the retardation of the process by the olefin.

The apparent activation energy of dehydrogenation processes is rather high: 170-190 kJ/mol (40-44 kcal/mol) for the conversion of *n*-butane to *n*-butylene; 105-140 kJ/mol (25-34 kcal/mol) for the dehydrogenation of *n*-butylene to butadiene; 152 kJ/mol (36 kcal/mol) for the dehydrogenation of ethylbenzene to styrene. This is responsible for the strong dependence of the rate of dehydrogenation on temperature; the ability to undergo dehydrogenation on oxide catalysts decreases in the following order: alcohols > amines > alkylbenzenes > paraffins; it increases with lengthening and branching of the carbon chain.

Hydrogenation processes are commonly carried out under conditions in which the equilibrium is strongly shifted to the right and the reverse dehydrogenation reaction may be neglected. Moreover, the saturated hydrogenation product has a low adsorption coefficient and is therefore usually omitted in the kinetic equation of the process. On the contrary, at a high pressure the sorption not only of the reactant but also of H_2 becomes significant, which gives:

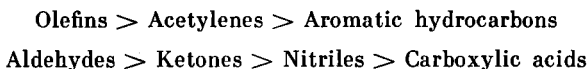
$$r = k \frac{P_A P_{H_2}}{1 + b_A P_A + b_{H_2} P_{H_2}}$$

With catalysts such as platinum, palladium and nickel, which vigorously sorb hydrogen, the reaction rate is independent of the partial hydrogen pressure at moderate temperatures (100 °C). The pressure begins to exert an effect on the reaction velocity only with increasing temperature—first to a fractional power and then linearly. There is also observed a distinct self-retardation of the reaction by the starting unsaturated compound; the apparent reaction order in unsaturated compound may be fractional or zero (say, in the hydrogenation of benzene).

The sorption of hydrogen on oxide catalysts is weaker than on metals, as a result of which the reaction rate usually depends linearly on the partial hydrogen pressure. This is responsible for the high efficiency of the use of high pressures and of an excess of hydrogen for the hydrogenation over oxide catalysts. In liquid-phase processes a high pressure has an additional effect, increasing the solubility of hydrogen in the reaction mass; linear, quadratic and even stronger dependences of the reaction rate on pressure have been reported. For instance, in the hydrogenation of ethyl laurate to lauryl alcohol over a chromite catalyst the reaction rate increases 7 times with the increase of pressure from 10 to 20 MPa and 28 times when the pressure increases to 30 MPa.

The temperature has a slight effect on the hydrogenation rate (in contrast to dehydrogenation). Normally, as the temperature increases by 30-50 °C the rate is approximately doubled, which corresponds to an activation energy of 21-42 kJ/mol (5-10 kcal/mol).

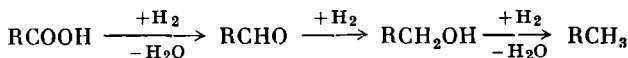
According to the tendency towards hydrogenation various classes of compounds may be arranged in the following order:



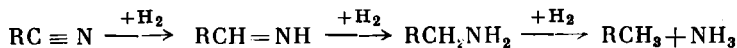
Selectivity of Hydrogenation and Dehydrogenation Reactions.

The selectivity of these reactions is important for two purposes: to prevent more complete conversions leading to a decrease in the yield of the end product and to effect a desired interaction (at a definite functional group) of the starting compound. Hence, the selectivity depends on the progress of consecutive and parallel reactions.

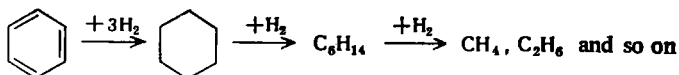
Many hydrogenation processes proceed via a series of intermediate steps. For example, carboxylic acids, aldehydes and ketones are reduced sequentially to alcohols and hydrocarbons:



and nitriles are reduced to imines, amines and hydrocarbons:

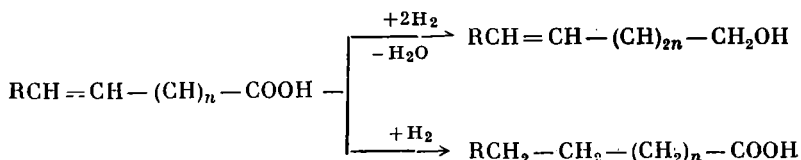


The further progress of these reactions may involve the hydrogenolysis of the organic compound with the formation of undesirable decomposition products:

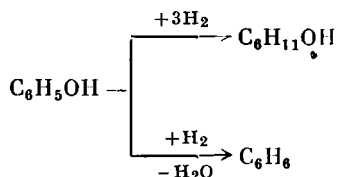


In all these cases, the reaction must be stopped at a certain stage, i.e., the reactants must be only partially hydrogenated and the subsequent conversions must be limited.

On the other hand, the molecule of the organic compound not infrequently contains two or more functional groups capable of hydrogenation; only one of these groups is to be attacked. For example, the hydrogenation of unsaturated acids can give an unsaturated alcohol or a saturated acid:



and from phenols there can be obtained an alcohol of the cyclohexane series or an aromatic hydrocarbon:



Dehydrogenation processes also involve a similar system of consecutive and parallel reactions, which are supplemented by the conversions initiated by a higher temperature as compared with hydrogenation. For example, the following processes occur: the cracking of the raw material, the hydrogenolysis under the action of the hydrogen formed and also polymerization, cyclization and dehydrocondensation reactions, which lead eventually to the formation of resinous compounds and coke, which deactivate the catalyst.

With the same catalyst the selectivity of the process depends on a number of factors, including the relative reactivity of organic compounds or individual functional groups and on their ability to be adsorbed by the catalyst surface. Often both factors act simultaneously or the first predominates over the second. As a result, for example, the double bonds of arylolefins are always hydrogenated first as compared with the aromatic ring, and the aldehyde groups are hydrogenated more rapidly than the ketonic groups. There are, however, cases where the reactivity towards chemisorption varies in the opposite direction. In such a case, the compound that is sorbed better displaces the reactant or the intermediate product from the catalyst surface and is hydrogenated first. This explains why acetylene and its homologues can be selectively hydrogenated to the corresponding olefins despite the higher reactivity of the olefins formed. The lower sorbability of the end products of the consecutive conversions (say, of alcohols upon hydrogenation of acids and carbonyl compounds and of amines upon hydrogenation of nitriles) allows the reaction to be accomplished with a better selectivity and a higher yield.

The sorption ability of catalysts with respect to various compounds or functional groups is an important factor, whose consideration in the choice of the catalyst serves as a powerful means of increasing the selectivity of the reaction. Metallic catalysts, especially platinum, palladium and nickel, have no specific ability to adsorb polar compounds and functional groups, and the adsorption of the reactant at carbon-carbon bonds occurs more readily on their surface. Therefore, unsaturated ketones, carboxylic acids and some derivatives of aromatic hydrocarbons are hydrogenated on metallic catalysts mainly across carbon-carbon bonds with retention of the polar group (the

hydrogenation of unsaturated fats and acids, the preparation of cyclohexanol from phenol). On the contrary, oxide catalysts, which have a polar crystalline lattice, have a specific sorption power with respect to the polar groups of organic compounds. A polyfunctional compound when being adsorbed on the surface of an oxide catalyst is found to be oriented to the polar group, as a result of which unsaturated and aromatic aldehydes, ketones, and carboxylic acids, nitro and other compounds are hydrogenated on oxide catalysts predominantly across oxygen-containing groups, the unsaturated or aromatic bonds remaining unaffected.

Regardless of the choice of the catalyst and other conditions, the selectivity of hydrogenation and dehydrogenation reactions is strongly influenced by the temperature. Usually, the lower the temperature, the more selectively can the process be effected across the more reactive groups or else the process can be stopped at a certain intermediate step. On the contrary, an increase in temperature favours more complete conversions. An essential point is that the undesirable side reactions of hydrogenolysis, cracking, dehydrocondensation, etc., have a higher activation energy than dehydrogenation or hydrogenation. For example, for the cracking of *n*-butane the activation energy is ≈ 250 kJ/mol (≈ 60 kcal/mol) and for its dehydrogenation to *n*-butylene it is only 168-184 kJ/mol (40-44 kcal/mol), which makes it possible to increase the selectivity by lowering the temperature. Since a decrease in temperature leads to a decrease in the rate of the process and in the capacity of the reactor, it follows that practically in each particular case one can find a region of optimum temperatures corresponding to a minimum cost. Additional limitations on the choice of this optimum are imposed by the reversibility of the hydrogenation-dehydrogenation reaction.

Finally, with other conditions being identical, the selectivity depends on the contact time, which determines the actual degree of conversion of the reactant. The closer it is to the equilibrium conversion, the more significant is the extent of the consecutive reactions of hydrogenation, hydrogenolysis, cracking or condensation, which lead to a decrease in selectivity. Therefore, for each hydrogenation and dehydrogenation process there is an optimum degree of conversion and an optimum contact time. Hydrogenation is normally carried out until a high degree of conversion (more than 90 percent) is reached, and the contact time varies from fractions of a minute to several hours, depending on the process. In a high-temperature dehydrogenation complicated by the reversibility of the reaction, the degree of conversion is sometimes as low as 20-40 percent, and the contact time ranges from fractions of a second to several seconds.

7.2. Chemistry and Technology of Dehydrogenation Processes

We will consider only three dehydrogenation processes that are of prime industrial importance:

(1) the dehydrogenation and oxidation of alcohols (the production of formaldehyde and some ketones);

(2) the dehydrogenation of alkylaromatic compounds (the production of styrene and its homologues);

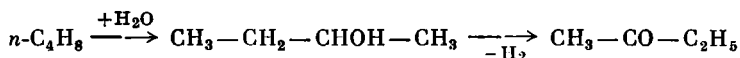
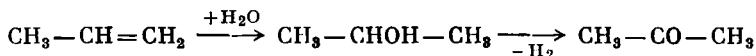
(3) the dehydrogenation of paraffins and olefins (the production of butadiene and isoprene).

7.2.1. Dehydrogenation and Oxidation of Alcohols

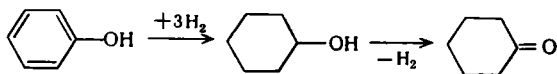
This route was once used to produce many aldehydes and ketones and also butadiene by the method proposed by S. V. Lebedev. Today this process remains to be of value only for the dehydrogenation of secondary alcohols and for the production of formaldehyde.

7.2.1.1. Dehydrogenation of Secondary Alcohols

Originally, ketones were made from secondary alcohols by way of oxidation in an excess of air catalyzed in the presence of metallic copper as the catalyst. Later, a more selective dehydrogenation process was predominantly employed. This process is used to produce a certain proportion of acetone and methyl ethyl ketone if the demand for these products is not satisfied by other methods (the cumene method or the oxidation of olefins; see pages 405 and 479). The first step in the synthesis of ketones is the hydration of olefins to alcohols (page 199) followed by dehydrogenation:



The same method is employed to produce a small proportion of cyclohexanone (page 416), in which the first step is the hydrogenation of phenol to cyclohexanol with the subsequent dehydrogenation:



As can be seen from Fig. 7.2, the equilibrium of the dehydrogenation of secondary alcohols lies strongly to the right even at 250-300 °C, but the process is carried out at 400-450 °C when the reaction

becomes practically irreversible. The catalysts used are copper, zinc oxide, silver on pumice, etc. The side reaction is the dehydration of the alcohol with the formation of the olefin, but the selectivity with respect to the ketone is high, reaching 98 percent. This allows the process to be operated at a 80-90 percent conversion with the recirculation of unconverted alcohol to dehydrogenation.

The high endothermicity of dehydrogenation requires the use of tubular reactors with the hot gases (produced by the burning of a gaseous or liquid fuel) being circulated in the intertubular space. A typical reaction unit for the dehydrogenation of alcohols is shown schematically in Fig. 7.5. The fuel gas supplied together with air

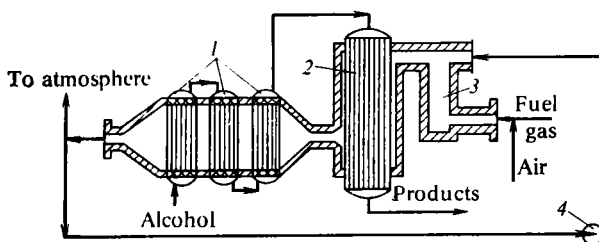


Fig. 7.5. Reaction unit for the dehydrogenation of alcohols:
1—vaporizer-superheaters; 2—tubular reactor; 3—combustion chamber; 4—gas blower.

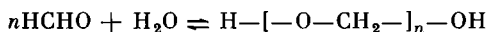
through special nozzles is burned in furnace 3. The temperature of the flue gases is too high, which is why they are diluted with the recycle gas (its circulation in the system is effected by gas blower 4). The alcohol is introduced into a system of vaporizer-superheaters 1, where it is heated to the required temperature by the partially cooled flue gases. The alcohol vapours are then passed into reactor 2, with the catalyst present in its tubes. The reaction mixture is heated by the hot flue gases present in the intertubular space, which compensates for the absorption of heat due to the endothermicity of the process. The reaction gases leaving the contact vessel are cooled in a cooler-condenser (not shown in Fig. 7.5), and in the case of volatile products they are additionally absorbed by water. The resultant condensate (and the aqueous solutions) are fractionated, the end product and unconverted alcohol being separated; the alcohol is recycled to dehydrogenation.

7.2.1.2. Production of Formaldehyde

The dehydrogenation or oxidation of primary alcohols is used only for the production of formaldehyde (from methanol).

Formaldehyde (methanal), HCHO , is in the anhydrous state a colourless gas possessing a pungent, penetrating smell (b.p. -19°C at

≈ 0.1 MPa). Upon storage it is readily polymerized and is often marketed in the form of a solid polymer—paraformaldehyde (paraform), which is easily depolymerized. *Paraform* is a linear polymer with repeating oxymethylene units (their number ranges from 8 to 100):

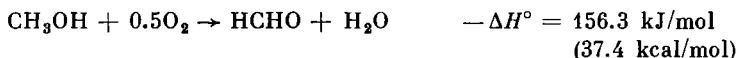


Formaldehyde mostly comes on to the market as a 37-percent aqueous solution, under the name of *formalin*. Formaldehyde is present in it in the form of the hydrate $\text{HCHO} \cdot \text{H}_2\text{O}$ and low-molecular polymers (polyoxymethylene glycols). In order to avoid a further stronger polymerization and the formation of a sediment, 7-12 percent (by weight) of methanol is added as a stabilizer.

Formaldehyde is produced on a very large scale and used for the production of a number of polymers (phenol-, carbamide- and melamine-formaldehyde polymers, polyformaldehyde) and also as an intermediate for the synthesis of isoprene, pentaerythritol, hexamethylene tetramine (urotropine) and other valuable compounds.

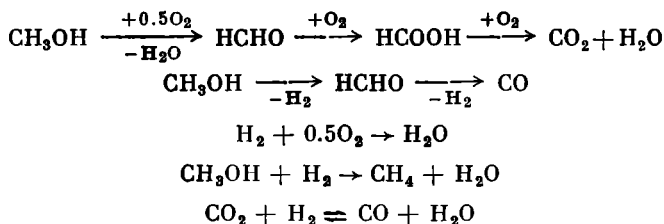
Apart from the oxidation of lower paraffins encountered earlier (page 407), the major proportion of formaldehyde is produced from methanol by two methods: by a combination oxidation-dehydrogenation process or by the oxidation of methanol in an excess of air.

The Combination Oxidation-Dehydrogenation Process. The dehydrogenation of primary alcohols, including methanol, is less favourable with respect to the equilibrium conditions and selectivity of the reaction as compared to secondary alcohols. For this reason and also in order to eliminate the endothermicity of the process, use was made of the combined dehydrogenation and oxidation of methanol:



The ratio of these reactions can be chosen such that the overall heat effect is only slightly positive but sufficient in order to compensate for the loss of heat to the surroundings and for the heat consumed for heating the starting mixture to the required temperature. In the practice of formaldehyde production, this situation occurs when the extent of oxidation is 55 percent and the extent of dehydrogenation is 45 percent, in which case the process can be carried out in adiabatic reactors having no heat-exchange surfaces. This is one of the advantages of the combination oxidation-dehydrogenation of alcohols. With the dehydrogenation-oxidation ratio indicated the starting vapour air mixture must contain ≈ 45 percent (by volume) of methanol, which is outside the upper explosive limit of methanol in air (34.7 percent by volume).

The principal reactions in the production of formaldehyde are accompanied by the side processes of more complete oxidation, dehydrogenation and hydrogenation, which lead to the formation of oxides of carbon, formic acid, water and methane:



The oxidative dehydrogenation is effected in a deficiency of oxygen, and the complete oxidation does not progress too far. At the same time, the dehydrogenation proper, which is initiated by oxygen, proceeds more rapidly and all the side reactions mentioned above are not so pronounced as during the dehydrogenation of primary alcohols. This permits the operation to be carried out at a higher temperature (500-600 °C), a faster reaction rate and a longer contact time (0.01-0.03 s). The yield of formaldehyde based on the starting material fed reaches 80-85 percent with the degree of methanol conversion being equal to 85-90 percent. It has been observed that addition of water to the methanol feed increases the yield and degree of conversion due probably to the decomposition of acetals. The catalysts used for the synthesis of formaldehyde by this method are metallic copper (in the form of a gauze or turnings) and silver on pumice. The latter catalyst has been found to be more efficient and is widely used in the industrial process.

The flow diagram of formaldehyde production by oxidative dehydrogenation of methanol is presented in Fig. 7.6. Methanol containing 10-12 percent of water is continuously fed from pressure tank 1 to vaporizer 2. Air freed of dust and other contaminants is also fed through a distribution device to vaporizer 2. The air is bubbled through the layer of aqueous methanol in the lower part of the vaporizer and becomes saturated with its vapours. One litre of the vapour-air mixture formed must contain ≈ 0.5 g of methanol. It is very important that this composition be kept constant in order to prevent the explosion hazard and to provide the normal occurrence of the process. The operation of the vaporizer system is therefore fully automated: the liquid level and the temperature (48-50 °C) in the vaporizer and also the rate of air feed are maintained constant, which provides the required temperature regime and degree of conversion in the adiabatic reactor.

The vapour-air mixture passes through the spray trap in the upper part of the vaporizer and then through superheater 3 and is led to

reactor 4 with the catalyst present in the middle part. The reaction gases are then immediately passed to cooler 5 beneath the catalyst bed (the cooler is built into the reactor), where the mixture is rapidly cooled and the decomposition of formaldehyde is prevented. Depending on the flowsheet used, cooling is effected by running water or the steam condensate, when the cooler functions as a generator of

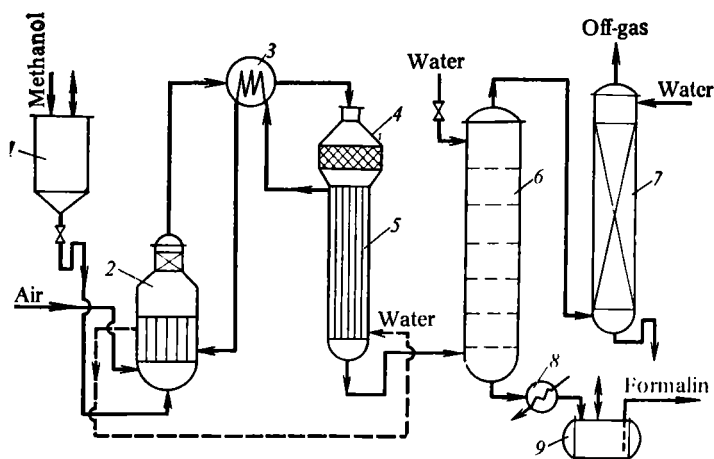


Fig. 7.6. Flow diagram of formalin production:

1—pressure tank; 2—vaporizer; 3—superheater; 4—reactor; 5, 8—coolers; 6—absorber; 7—scrubber; 9—collector.

low-, medium- or even high-pressure steam. The steam produced (or hot water) is used to superheat the mixture feed in heat exchanger 3 and to heat vaporizer 2.

The cooled reaction gases are passed to absorber 6 designed in the form of a tray column; the liquid on the trays is cooled by internal or external coolers (not shown in Fig. 7.6). The absorber is refluxed by such an amount of water that 36-37 percent formalin is obtained in the still. The product absorption and separation steps are carried out in two different ways.

In one method, formaldehyde and the unreacted methanol contained in the products in an amount sufficient for the stabilization of formaldehyde are absorbed in the absorber. In this case, the upper tray of the absorber is cooled by brine, and column 7 is used for the sanitary purification of the gas, whereas the production of methanol-free formalin (required sometimes for various purposes) needs a methanol recovery unit.

In the second method, formaldehyde is practically the only compound to be absorbed in the absorber and column 7 is used for the

absorption of methanol, which is distilled off from the water and returned to the reaction. In either case, the formalin from the still of absorber 6 is cooled in cooler 8 and collected in collector 9.

Oxidation of Methanol to Formaldehyde. This is a new process that has only recently been developed to the commercial stage. It is carried out in an excess of air at 350–430 °C and ordinary pressure over an iron-molybdenum oxide catalyst, which functions by the redox mechanism involving the lattice oxygen. The process is noted for high degree of methanol conversion (99 percent) and high selectivity (95–96 percent) and also for high exothermicity, which is why

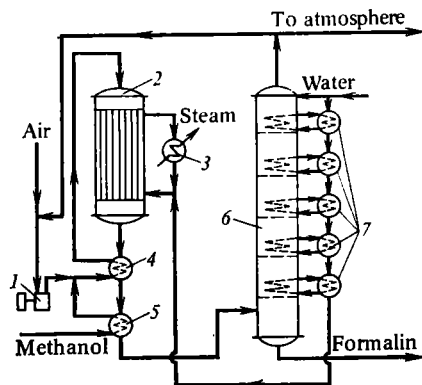


Fig. 7.7. Flow diagram of formaldehyde production by oxidation of methanol:

1—turbocompressor; 2—reactor; 3—steam generator; 4, 5—heat exchangers; 6—absorber; 7—external coolers.

tubular reactors cooled by a suitable heat-exchange medium has to be used. The heat-exchange medium commonly used for this purpose is water boiling under pressure or an intermediate heat-exchange agent, which is used to produce steam with a pressure of up to 3 MPa. This steam is sufficient for all the needs of the plant, including the driving of the air turbocompressor; the excess steam (1.8 tons per 1 ton of formaldehyde) is used outside the plant. Despite the higher capital cost and the large amount of metal used for the reaction unit and also the lower capacity of the catalyst, the method of methanol oxidation finds an ever increasing use owing to the low

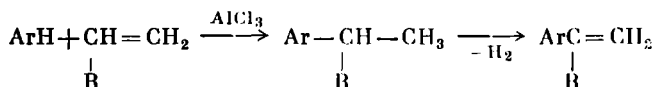
consumption of the raw material, the high degree of methanol conversion and the high power-technological efficiency of the production.

A simplified flow diagram of the process is shown in Fig. 7.7. Fresh air before being fed into turbocompressor 1 is diluted with the recycle off-gas, as a result of which the explosion hazard of mixtures with methanol is reduced and the content of CH_3OH in the gas is brought to 10–12 percent (by volume). The methanol is vaporized in heat exchanger 5 (by the heat of the reaction gases) and is mixed with air and the mixture is heated in heat exchanger 4, following which it is fed to tubular reactor 2. The reaction heat is removed with the aid of an intermediate heat-exchange medium, which produces steam (2–3 MPa) in steam generator 3. This steam is used to drive the turbocompressor; the steam is then utilized outside the plant.

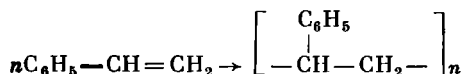
The hot reaction gases give up their heat in heat exchangers 4 and 5 to the reactants and pass to absorber 6 refluxed by water, which absorbs formaldehyde with the formation of 37-percent formalin. The heat of absorption is utilized in external coolers 7, where demineralized water to be used for steam generation is heated. Part of the gas leaving the absorber is recycled and the remainder passes through the furnace (not shown in the flow diagram) and vented to the atmosphere. No wastes, sewage or harmful discharge are involved in the production.

7.2.2. Dehydrogenation of Alkylaromatic Compounds. Production of Styrene and Its Homologues

The dehydrogenation of alkylaromatic compounds is a very important industrial process used for the production of styrene and its homologues. The dehydrogenation step completes the two-stage operation which starts with the alkylation of benzene or its homologues by an olefin encountered earlier (page 263):



Styrene (vinylbenzene), $\text{C}_6\text{H}_5 - \text{C} = \text{CH}_2$, is a colourless liquid (b.p. 145.2 °C at 0.1 MPa). It polymerizes on heating or under the action of initiators with the formation of a solid polymer—polystyrene:



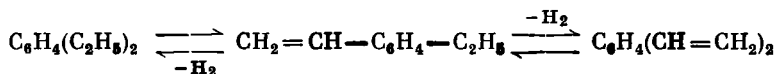
Polystyrene possesses good insulating properties and high chemical stability. It is used for the fabrication of parts for electrical and radio equipment, foam plastics, general-purpose plastic articles. Extensive use is made of copolymers of styrene with acrylonitrile, divinylbenzene and N-vinylcarbazole. One of the most important outlets for styrene is the production of synthetic rubbers (SBR) by copolymerization of styrene with butadiene.

α-Methylstyrene, $\text{C}_6\text{H}_5 - \text{C}(\text{CH}_3) = \text{CH}_2$, is a colourless liquid which boils at 161–162 °C. It polymerizes more slowly than styrene, which facilitates its recovery from the reaction mixtures and its storage. In the production of synthetic rubbers (by copolymerization with butadiene) α-methylstyrene is used on the same scale as styrene, but the amount used for the manufacture of plastics is limited.

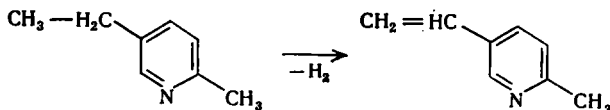
Of the other vinyl monomers of the aromatic series, mention should be made of *vinyltoluenes*, $\text{CH}_3 - \text{C}_6\text{H}_4 - \text{CH} = \text{CH}_2$, which are mixtures consisting of 65 percent of the *meta*-isomer and 35 percent of the *para*-isomer. They are produced from a mixture of ethyltoluenes

formed by the ethylation of toluene. The replacement of styrene by vinyltoluenes is of interest for the expansion of the range of raw materials (toluene is more available and cheaper than benzene) and also for the modification of the properties of polymers. There are data indicating the production and applications of *chlorostyrenes* ($\text{Cl}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2$), *vinyl-naphthalene* ($\text{C}_{10}\text{H}_7-\text{CH}=\text{CH}_2$) and other analogous compounds.

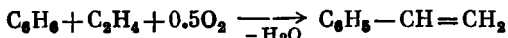
Divinylbenzene, $\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2)_2$ (a mixture of isomers) is used in the production of ion-exchange resins—its insoluble copolymers with styrene, into which ion-exchange groups are introduced. Divinylbenzene is made from a mixture of diethylbenzene isomers; the dehydrogenation reaction proceeds via the intermediate formation of vinyl-ethylbenzene, which is returned to dehydrogenation together with the unconverted diethylbenzene:



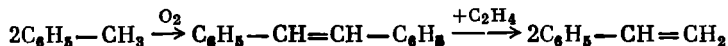
A further valuable monomer produced by the dehydrogenation of the corresponding dialkylpyridine is *5-vinyl-2-methylpyridine*:



The most important of the compounds listed above is styrene. An additional source of styrene has been recently provided by the combined production of propylene oxide and styrene via ethylbenzene hydroperoxide (page 474). New interesting methods have been developed: the oxidative coupling of benzene with ethylene in the presence of a palladium catalyst



and the oxidative condensation of toluene to stilbene followed by the disproportionation of stilbene with ethylene:



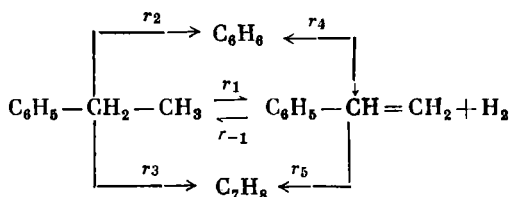
The method of dehydrogenation of alkylbenzenes is, however, the major process for the production of arylolefins.

Basic Regularities of the Process. As can be seen from the above-considered thermodynamic relationships (page 493), the equilibrium of the dehydrogenation of alkylbenzenes is unfavourable for the production of arylolefins. Therefore, at a permissible temperature (600–630 °C), for the equilibrium degree of conversion to be increased at atmospheric pressure the hydrocarbons are diluted with steam in

a mass ratio ranging from (2.5-3):1 in the production of styrene and α -methylstyrene to (6-8):1 for the synthesis of divinylbenzene.

The heterogeneous catalysts used in the past were styrene catalysts based on ZnO, but the present practice is to use only iron-oxide catalysts containing 55-80 percent Fe_2O_3 , 2-28 percent Cr_2O_3 , 15-35 percent K_2CO_3 with addition of some oxides. Potassium carbonate is said to contribute to the self-regeneration of the catalyst due to the conversion of carbonaceous deposits by steam. The catalyst operates continuously for 1-2 months, after which it is regenerated by burning off the coke with air; the overall service life of the catalyst is 1-2 years.

During the dehydrogenation of alkylbenzenes a number of side reactions occur on these catalysts. For example, ethylbenzene forms benzene and toluene; the scheme of the conversions involved is as follows:



The by-products formed in the dehydrogenation of isopropylbenzene are ethylbenzene, styrene, toluene and benzene; the by-products formed from diethylbenzene are ethylbenzene, styrene, ethyltoluene, methylstyrene, etc. The resulting gas therefore contains (in addition to hydrogen) methane, ethylene, ethane and (as a result of the conversion of coke) oxides of carbon.

The selectivity of the dehydrogenation of alkylbenzenes depends on the temperature, steam dilution and the degree of conversion. From the above-given scheme of ethylbenzene dehydrogenation it is clear that the differential selectivity with respect to styrene is expressed by the following equation:

$$\varphi_{\text{st}} = \frac{d[\text{Styrene}]}{d[\text{Ethylbenzene}]} = \frac{1 - \frac{r_4 + r_5}{r_1 - r_{-1}}}{1 + \frac{r_2 + r_3}{r_1 - r_{-1}}}$$

It can be seen that the selectivity drops especially sharply when the actual degree of conversion approaches the equilibrium conversion, i.e., when r_{-1} is close in value to r_1 . Dilution with steam, while increasing the equilibrium degree of conversion, favours the increase of the selectivity, but the effect of the temperature is dual. On the one hand, an increase in temperature also leads to an increase in the equilibrium degree of conversion, but on the other hand, some side

reactions become more significant, including the coking of the catalyst, which lowers its activity. Therefore, there is a certain optimum range of temperatures for dehydrogenation reactions: 580-600 °C for ethylbenzene and 530-550 °C for more reactive isopropylbenzene. Besides, for each extent of steam dilution and each temperature there is an optimum degree of conversion determined by economic considerations. An appropriate choice of the catalyst and reaction conditions makes it possible to attain a selectivity of ≈ 90 percent.

Reaction Unit. The reaction unit for the dehydrogenation of alkylbenzenes may be constructed in various ways. One of the variants is a tubular reactor heated by the flue gas which is similar to the one

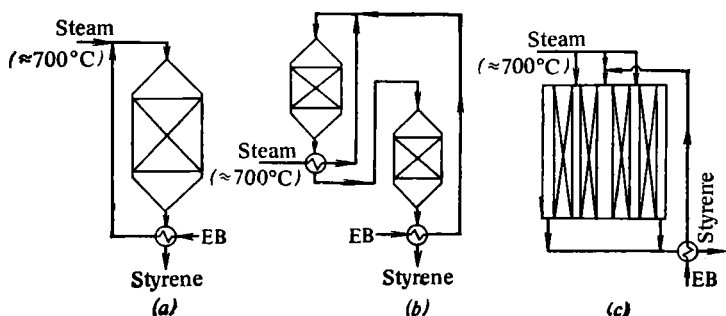


Fig. 7.8. Reaction units for dehydrogenation of ethylbenzene:

a—adiabatic-type reactor; *b*—unit consisting of two reactors with intermediate heating of the mixture; *c*—reactor with several catalyst beds and with sectional feed of superheated steam.

shown in Fig. 7.5. An advantage of this reactor is the near-isothermal temperature profile, which provides an increased degree of conversion at a good selectivity. Because of the large amount of metal and high capital cost required for such a reactor, other vessels have been designed—fixed-bed reactors having no heat-exchange surfaces (Fig. 7.8*a*). They operate under adiabatic conditions and the reaction mixture is cooled slowly; the steam in such reactors plays the role of heat-retaining medium, which prevents the mixture from being excessively cooled. When styrene is produced in a single adiabatic reactor, the usual degree of conversion of ethylbenzene is ≈ 40 percent; the temperature at the entrance and exit from the catalyst bed varies from 600-620 to 540-570 °C with the volume flow rate for liquid ethylbenzene being 0.2-0.3 h⁻¹. The shortcomings of such a reactor are the excessive cooling of the mixture, the shift of the equilibrium to the undesirable side and the associated decrease of the reaction rate and selectivity. The degree of conversion cannot be increased considerably since this will increase the steam consumption.

The reaction unit of new plants has been designed so as to effect the process under near-isothermal conditions and to take better account of the specificity of the reaction equilibrium. One of such units (Fig. 7.8b) is equipped with two reactors (or two catalyst beds); the mixture cooled in the first reactor is heated by superheated steam to 600-630 °C before being fed to the second reactor. The reactor shown in Fig. 7.8c has two or three ring-shaped catalyst beds; all of the ethylbenzene and only part of the steam are fed into the first bed. An additional amount of superheated steam is introduced into

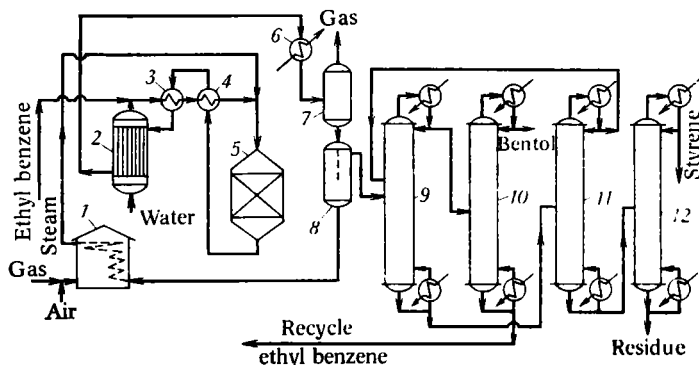


Fig. 7.9. Flow diagram of styrene production:

1—tubular furnace; 2—waste-heat boiler; 3, 4—heat exchangers; 5—reactor; 6—coolers
7, 8—separators; 9, 10, 11, 12—fractionating columns.

the space between the catalyst beds; with its aid the temperature of the mixture is increased and the mixture is diluted in a stepwise manner and brought out of its equilibrium state, which favours the increase of the rate and selectivity of the reaction. In these new plants, with the high selectivity being retained (89-90 percent) the degree of conversion and the intensity of the process are increased (the conversion is 60-75 percent and the volume flow rate is 0.5-0.6 h⁻¹) and the steam consumption is reduced.

Flow Diagram of Styrene Production. The flow diagram of styrene production is shown in Fig. 7.9. Fresh and recycle ethylbenzene together with a small amount of steam are fed into vaporizer 3 and heat exchanger 4, where the vapours are heated by the hot reaction mixture to 520-530 °C. Superheated (700 °C) steam is generated in tubular furnace 1, from which it is sent for mixing with ethylbenzene vapours and then to reactor 5.

The reaction mixture leaving the reactor has a temperature of 560 °C. It gives up its heat first in heat exchangers 4 and 3 for heating ethylbenzene and then in waste-heat boiler 2 for producing low-pressure steam (this steam is used for the evaporation and dilution of ethylbenzene before it is fed into heat exchanger 3). The vapour-air

mixture is then cooled in a system of coolers 6 by water and brine and the condensate is separated from the gas in separator 7, following which the gas is led into the fuel gas line. Then, the condensate is separated in separator 8 into an aqueous and an organic phase. The organic phase, which contains unconverted ethylbenzene, styrene and by-products (benzene, toluene), is called the furnace oil. It is passed to fractionation, which is carried out with account taken of the tendency of styrene towards thermal polymerization. In order to prevent polymerization, inhibitors are used (hydroquinone, etc.), the distillation temperature is lowered due to the use of vacuum, and the time of residence of styrene-containing liquids in the columns is reduced through the use of packings, special stills, etc. The fractionation is also complicated by the closeness of the boiling points of ethylbenzene (136 °C) and styrene (145 °C).

The furnace oil is led to vacuum-fractionation column 9, where benzene, toluene and a greater proportion of ethylbenzene are distilled from it. This distillate is split in column 10 into a benzene-toluene fraction (bentol) and ethylbenzene, which is returned to dehydrogenation. The still liquid of column 9 which contains styrene is run to vacuum-fractionation column 11, where the residual ethylbenzene is distilled off together with a certain proportion of styrene. This mixture is returned for fractionation to column 9. The still liquid of column 11 is subjected to final fractionation in vacuum column 12. The distillate is 99.8-percent styrene, which satisfies the quality requirements. The heavy residue containing styrene polymers is left in the still of the column. This residue is subjected to fractionation in two distillation columns (not shown in Fig. 7.9) to isolate the more volatile compounds, which are returned to column 12 for fractionation.

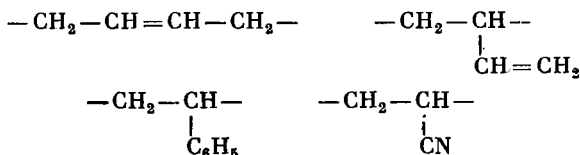
A method of oxidative dehydrogenation of ethylbenzene is being developed, in which a mixture of steam, ethylbenzene vapours and oxygen is passed through metal oxide heterogeneous catalysts at ≈ 600 °C. This makes it possible to eliminate the irreversibility and endothermicity of the reaction, to increase the conversion of ethylbenzene with a good selectivity being retained and to reduce the power consumption. The method is analogous to the method of oxidative dehydrogenation of olefins to be described at a later time (page 522).

7.2.3. Dehydrogenation of Paraffins and Olefins. Production of Butadiene and Isoprene

The dehydrogenation of paraffins and olefins, namely *n*-butane, *n*-butylenes, isopentane, and isoamylenes, is of great practical value in the production of the basic monomers for synthetic rubber—1,3-butadiene and isoprene.

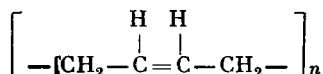
1,3-Butadiene (divinyl), $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, is a colourless gas under ordinary conditions, which is condensed into a liquid at -4.3°C (atmospheric pressure). 1,3-Butadiene forms explosive mixtures with air within the concentration limits of 2.0-11.5 percent (by volume) and is slightly toxic, irritates the eyes and has a narcotic effect.

1,3-Butadiene is the basic monomer for the production of synthetic rubbers. The radical-chain copolymerization of butadiene with styrene, α -methylstyrene or acrylonitrile gives copolymers, whose macromolecules contain randomly alternating units of the starting materials:



Butadiene is chemically characterized by addition at 1,4- or 1,2-positions.

Especially valuable properties are exhibited by stereoregular *cis*-butadiene rubber. It is produced by the polymerization of butadiene in the presence of organometallic compounds and Ziegler complex catalysts ($\text{AlR}_3 \cdot \text{TiCl}_4$, etc.). In the resultant polymer, butadiene is bound preferentially at the 1,4-position with the *cis*-arrangement of hydrogen atoms at the double bond:

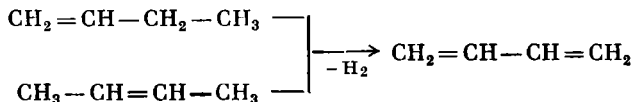


Most of these rubbers are general-purpose materials and are used for the manufacture of car tires and inner tubes, shoes and various technical articles. Butadiene-nitrile rubber is noted for high gasoline and oil resistance and is used for the fabrication of special-purpose items.

The problem of the production of synthetic rubber and the basic monomer for it, 1,3-butadiene, has long attracted the attention of scientists and engineers. The most popular methods used in the past for the production of 1,3-butadiene were the Ostromyslensky method (from acetaldehyde), the Lebedev process (from ethyl alcohol) and the Reppe process (from acetylene and formaldehyde); today only three methods are of commercial interest.

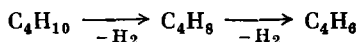
1. The production of butadiene from the C_4 fraction of the products of pyrolysis of liquid petroleum fractions. This method has already been described (see Chapter 1). It is the most economical and is expected to satisfy the 40-50 percent of the total demand for this monomer.

2. The dehydrogenation of the *n*-butylene fraction derived from the pyrolysis and catalytic-cracking products after the extraction of butadiene and isobutylene:



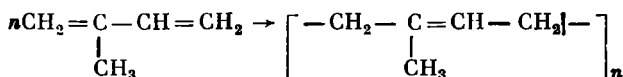
Economically, this method ranks second.

3. The dehydrogenation of *n*-butane derived from casinghead gases:

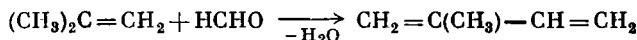


Isoprene (2-methyl-1,3-butadiene), $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$, is a colourless liquid, which boils at 34 °C. It forms explosive mixtures with air within the concentration limits of 1.7-11.5 percent (by volume). Isoprene is well known as the basic structural unit of natural rubber.

Isoprene is more valuable than butadiene for the production of synthetic rubber, but because of the greater difficulty of its production the switch was made to butadiene. Isoprene is used for the manufacture of butyl rubber by way of the copolymerization of isobutylene with a small amount of isoprene. Isoprene has only recently found its chief outlet in the production of polyisoprene rubber of a stereoregular structure made by the polymerization of isoprene in the presence of organometallic catalysts in the same way as *cis*-butadiene rubber:



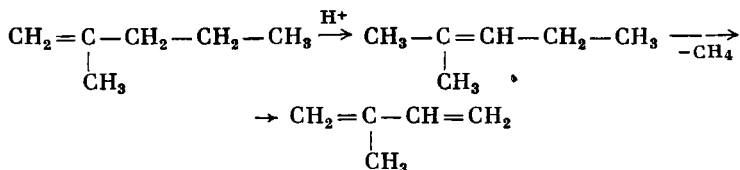
Isoprene is made by the same three methods used for the production of butadiene (the separation from pyrolysis products; the dehydrogenation of the isoamylenes fraction; and the dehydrogenation of isopentane), but because of the complexity of the composition and considerable difficulties encountered in the separation of the starting or resulting fractions, synthetic methods are still of industrial significance. The most important of these is the synthesis from isobutylene and formaldehyde:



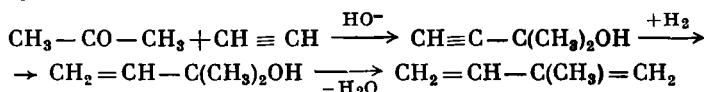
which will be described in detail in Chapter 9. Another route proceeds via isopentane hydroperoxide and involves the epoxidation of isoamylenes by this hydroperoxide and dehydration; it has already been described (Chapter 6).

A promising route to isoprene is the synthesis via the propylene dimer, which is obtained with the aid of aluminium alkyls. In the presence of acid catalysts this dimer (2-methyl-1-pentene) isomerizes

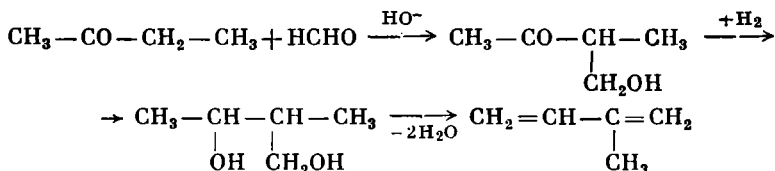
to 2-methyl-2-pentene, which is capable of losing CH_4 upon pyrolysis:



Two other methods are less interesting—from acetone and acetylene according to the Favorsky reaction:



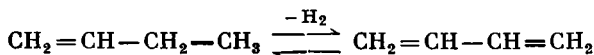
and from methyl ethyl ketone and formaldehyde:



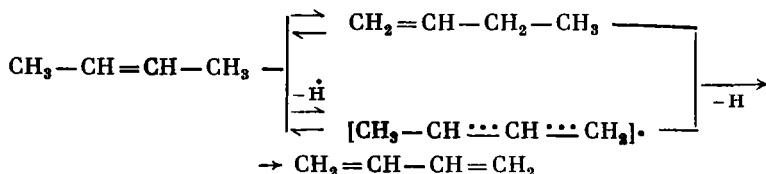
7.2.3.1. Dehydrogenation and Oxidative Dehydrogenation of Olefins

Dehydrogenation of Olefins. This process is thermodynamically unfavourable to the same extent as the dehydrogenation of alkyl-aromatic hydrocarbons (page 494). Therefore, in this case too the equilibrium degree of conversion at a permissible temperature ($\approx 600^\circ\text{C}$) can be achieved by diluting the reacting mixture with steam.

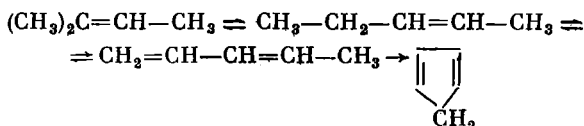
n-Butylenes or isoamylenes to be subjected to dehydrogenation are mixtures of isomers, regardless of their origin (from the products of pyrolysis, cracking or dehydrogenation of the corresponding paraffins); only α -olefins are directly subjected to dehydrogenation:



The β -isomers must be preliminarily isomerized with the migration of the double bond or with the formation of the surface radical having delocalized electrons:



Apart from the major reactions, the dehydrogenation also involves side processes of cracking, skeleton isomerization and coke formation. The cracking process of olefins gives methane and C_2 and C_3 hydrocarbons. The isomerization of *n*-butylene gives isobutylene, but this reaction is especially undesirable for isoamylenes: the *n*-amylenes formed are further dehydrogenated to 1,3-pentadiene (piperylene), which can then undergo ring closure to form cyclopentadiene:

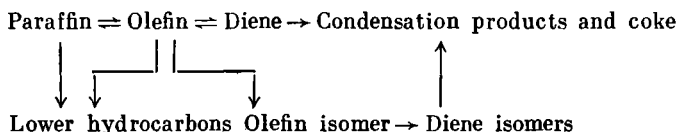


Apart from lowering the selectivity of the process, the negative role of the last-named reactions is that they involve the formation of impurities which complicate the purification and recovery of the end products.

The dehydrogenation of olefins yields condensation products and coke. It is believed that they are formed mainly from dienes which are liable to condensation reactions leading to the formation of cyclic systems (the diene synthesis followed by the dehydrocondensation of aromatic compounds).

Finally, the dehydrogenation of olefins also involves (owing to the hydrogen formed) the formation of a small amount of paraffins, which are cracked more readily than the corresponding olefins. Part of the hydrocarbons and some of the coke undergo conversion by steam, as a result of which the gas also contains oxides of carbon.

Thus, the scheme of conversions involved in the dehydrogenation of olefins is as follows:



Thus, the process involves parallel and consecutive routes to by-products; just as in the case of the dehydrogenation of alkylaromatic hydrocarbons, here the selectivity also increases with decreasing temperature (because of the high activation energy of the side reactions) and with decreasing degree of conversion; the choice of these process parameters is dictated by economical considerations.

According to what has been said above, the catalysts used for the dehydrogenation of olefins must preferentially accelerate the dehydrogenation and isomerization with the migration of the double bond, but they must be relatively inactive with respect to the cracking, skeleton isomerization and coke formation. At present, the best catalysts are calcium-nickel-phosphate catalysts. Their composition

corresponds to the formula $\text{Ca}_8\text{Ni}(\text{PO}_4)_6$; the promoter is Cr_2O_3 added in an amount of ≈ 2 percent; they are marketed in moulded forms for use in the fixed bed. A characteristic feature of these catalysts is that they become rapidly coked and lose their activity, and therefore the coke formed has often to be burned off. The dehydrogenation and catalyst regeneration periods alternate every 15-30 min and in between the reactor is blown by steam.

The dehydrogenation is carried out by diluting the starting mixture with steam in a volume ratio of 20:1 at a volume flow rate of the

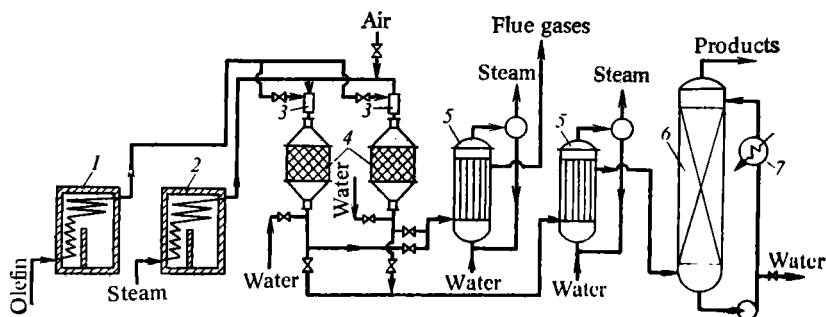


Fig. 7.10. Flow diagram of dehydrogenation of olefins:

1, 2—tubular furnaces; 3—mixers; 4—reactors; 5—waste-heat boilers; 6—scrubber; 7—cooler.

gaseous hydrocarbon of $150\text{--}200\text{ h}^{-1}$ and a total pressure only slightly above atmospheric (in order to overcome the hydraulic drag of the catalyst bed and of the subsequent vessels). The optimum temperature upon dehydrogenation of *n*-butylenes is $600\text{--}650^\circ\text{C}$; the degree of conversion is 40-45 percent and the selectivity with respect to butadiene is 85 percent. For isoamylene, which is more reactive and more liable to undergo side reactions, the dehydrogenation temperature is $550\text{--}600^\circ\text{C}$, in which case the degree of conversion is 40 percent and the selectivity 82-84 percent.

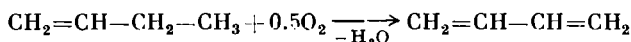
The process is carried out in fixed-bed reactors having no heat-exchange surfaces and operating under adiabatic conditions (just as in the dehydrogenation of alkylaromatic hydrocarbons). The steam here also plays the role of a heat-exchange medium which prevents the mixture from being excessively cooled (the temperature gradient between the entrance and exit from the catalyst bed is $30\text{--}40^\circ\text{C}$).

The flow diagram of the dehydrogenation of olefins is given in Fig. 7.10. The olefinic fraction and steam superheated in tubular furnaces 1 and 2 to 500 and 700°C , respectively, are mixed and the required temperature is provided at the reactor inlet. Because of the rapid alternation of the dehydrogenation and catalyst-regeneration periods, reactors 4 operate in pairs: the dehydrogenation of ole-

fin takes place in one reactor and the regeneration of the catalyst by an air-steam mixture in the other. Upon completion of each of these periods the reactors are blown off for a short time by steam (the cycles are switched automatically using control computers). The heat of the regeneration gases and of the reaction gas is used for the generation of steam, after which the regeneration gases are vented to the atmosphere and the reaction gas is sent to the separation unit. The lower and higher hydrocarbons are separated first (by fractionation at a low pressure); then, butadiene and isoprene are recovered, respectively, from the C_4 and C_5 fractions by the methods that have already been described (see Chapter 1). The unconverted olefins are recycled to dehydrogenation.

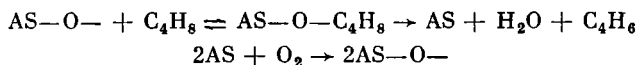
Oxidative Dehydrogenation of Olefins. The above dehydrogenation of olefins has substantial disadvantages: the cyclic operation of the catalyst and the reaction unit; the relatively low degree of conversion and selectivity; the consumption of a large amount of power. This has stimulated the search for more efficient methods for the production of dienes from olefins.

The most promising method is the oxidative dehydrogenation of olefins, in which oxygen or air (to combine hydrogen into water) is introduced into the reaction mixture:



This eliminates the reversibility of the dehydrogenation reaction and removes the thermodynamic limitations on the degree of conversion of the olefin; the adiabatic process becomes exothermic which is more convenient to operate. Moreover, just as in other oxidation reactions, the highly undesirable coke formation is eliminated and the catalyst functions for a longer time without being regenerated.

The catalysts used for the oxidative dehydrogenation of olefins are the following oxide compositions: Bi + Mo, Bi + Mo + P, Bi + W, Fe + Sb, etc. These catalysts are all active at 400-600 °C and operate by the redox mechanism (page 444) involving the oxygen of the crystalline lattice: (AS stands for an active site of the catalyst):



In one of the variants of the process, in order to prevent the action of molecular oxygen on the olefin, the dehydrogenation of the olefin by the oxidized catalyst and the oxidation of the reduced catalyst by air are carried out in two different reactors containing a fluidized bed of the circulating catalyst. In another system that has already been developed to the commercial stage, the dehydrogenation and oxidation are carried out jointly in a single fixed-bed reactor. In all these cases, the olefin must be diluted with steam in a volume ratio of 1:5 to 30:1, the degree of conversion attained is 70-80 percent

and the selectivity is 90-95 percent with respect to butadiene and ≈ 85 percent with respect to isoprene.

The flow diagram of the oxidative dehydrogenation of *n*-butylene is given in Fig. 7.11. Steam and air are mixed and superheated in tubular furnace 1 to 500 °C. The butylene fraction is introduced into this mixture before it is fed into reactor 2. The process is effected over a fixed catalyst bed under adiabatic conditions at 400-500 °C and ≈ 0.6 MPa. The heat of the hot reaction gases is used in waste-heat

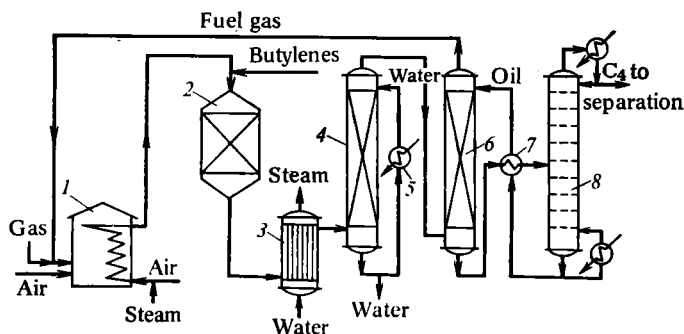


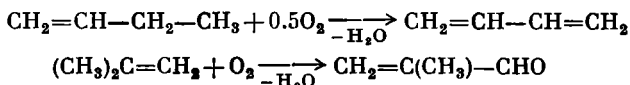
Fig. 7.11. Flow diagram of oxidative dehydrogenation of *n*-butylene to butadiene:

1—tubular furnace; 2—reactor; 3—waste-heat boiler; 4—scrubber; 5, 7—coolers; 6—absorber; 8—stripper.

boiler 3 for the generation of steam (an advantage of the operation at elevated pressure is that steam can be produced by using the heat released during the condensation of the steam-diluent of the reaction gases, in contrast to the operation at atmospheric pressure in the dehydrogenation of ethylbenzene and *n*-butylenes). The gas is then cooled by water in scrubber 4 equipped with cooler 5 and washed by a mineral oil in absorber 6, where the C_4 hydrocarbons are absorbed. The cracked products, nitrogen and residual oxygen are withdrawn from the top of the absorber and used as a fuel gas in tubular furnace 1. The saturated oil from absorber 6 is led to stripping column 8, where the absorbent oil is regenerated and returned after being cooled to absorption. The C_4 fraction from the top of stripping column 8 contains ≈ 70 percent of butadiene. Pure butadiene is then recovered from it by the methods described earlier, and the unconverted *n*-butylenes are recycled to oxidative dehydrogenation.

A further method consists of the oxidation and oxidative dehydrogenation of a mixture of *n*-butylenes with isobutylene; these compounds need not be separated (the production cost is thus reduced). The same catalysts after addition of air and dilution with steam are used to dehydrogenate *n*-butylenes to butadiene (selectivity 90 per-

cent) and to oxidize isobutylene to methacrolein (selectivity 80-90 percent):



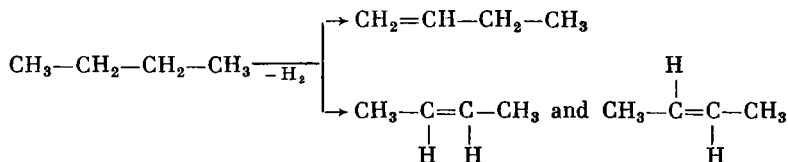
The same butylene mixture gives butadiene and methacrylonitrile under the conditions of oxidative ammonolysis (ammonoxidation). The scope of the future development of the joint oxidation and oxidative dehydrogenation of *n*-butylenes and isobutylene will apparently depend on the demand for methacrylates.

7.2.3.2. Dehydrogenation of Paraffins

When the production of dienes uses the corresponding paraffins (*n*-butane or isopentane) as the feedstock, the process is carried out in two ways: (1) as a two-stage process (the first step is the dehydrogenation of the paraffin to the olefin and the second is the dehydrogenation or oxidative dehydrogenation of the olefin to the diene); (2) as a single-step process.

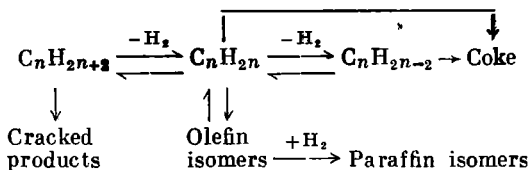
Dehydrogenation of Paraffins to Olefins. The first step of the two-stage synthesis of dienes is thermodynamically more favourable than the dehydrogenation of alkylaromatic hydrocarbons and olefins (page 493). Therefore, at a permissible temperature ($\approx 600^\circ\text{C}$) there is no need to reduce the partial pressure and the process is effected without diluents at a pressure only slightly above atmospheric.

The dehydrogenation of C_4 and C_5 paraffins yields a mixture of isomeric olefins; for example, butane gives 1-butene and *cis*- and *trans*-2-butenes:



Besides, the reaction gives rise to the corresponding dienes but they are formed in small amounts since the reaction conditions are thermodynamically unfavourable for their formation. Just as in the dehydrogenation of olefins, the side reactions involved are cracking, isomerization and coke formation. Paraffins are more reactive than olefins towards decomposition reactions, which is why the lower hydrocarbons (CH_4 , C_2H_4 , C_2H_6 , etc.) are formed in larger quantities. It is believed that the isomerization occurs mainly with olefins and the isomeric olefins (isobutylene or *n*-amylene) undergo partial hydrogenation. The reaction products therefore contain isomeric paraffins (isobutane and *n*-pentane). Just as with the dehydrogenation of olefins, there is formed a large amount of coke as a result of the

condensation of dienes and decomposition of hydrocarbons into carbon and hydrogen. The scheme of conversions in this process is as follows:



The catalysts to be used for the dehydrogenation of paraffins must accelerate the principal reaction but their activity with respect to cracking, isomerization and coke-formation must be as low as possible. The best catalysts are chromia-alumina catalysts on the basis of Al_2O_3 and containing 10-40 percent of Cr_2O_3 and 2-10 percent of oxides of alkali metals (Na_2O , K_2O , BeO); these oxides neutralize the acid centres of Al_2O_3 , which cause cracking and isomerization. These catalysts are highly susceptible to moisture and the starting C_4 and C_5 fractions therefore must not contain more than 1 mg of water vapour in 1 m³.

Chromia-alumina catalysts are active in the dehydrogenation of *n*-butane and isopentane at 500-650 °C, but an increase in temperature leads to an intensive development of side reactions with a higher activation energy. The optimum temperature is said to be 560-590 °C for the dehydrogenation of *n*-butane and 530-560 °C for the dehydrogenation of more reactive isopentane. The selectivity falls off with increasing conversion of the paraffin feed (mainly because of the retardation of the dehydrogenation reaction as the equilibrium is approached), and therefore it is limited to 40-45 percent. Under the conditions indicated the selectivity of the process to *n*-butylene is ≈ 75 percent (plus 6-7 percent to butadiene) and ≈ 70 percent to isoamylene (plus 4-5 percent to isoprene). Under the conditions indicated above the chromia-alumina catalysts are still coked and the coke deposits must be burned off periodically by air at 600-650 °C.

Because of the high endothermicity of the process and of the operation being carried out in the absence of a diluent-heat exchange agent, tubular reactors heated by flue gases were used originally, with alternating cycles of paraffin dehydrogenation and catalyst regeneration. Later, systems with a fluidized microspherical catalyst bed became popular. Such systems combine the regenerative principle of heat utilization with a continuous catalyst regeneration, which is analogous to that used in catalytic cracking (page 49). The deactivated catalyst leaves the reactor and passes to the regeneration unit, where the coke is burned off by air. Because of the exothermicity of the last reaction, the catalyst warms up and is again led to the reactor, where it performs an additional function as a heat-exchange

medium to compensate for the heat lost for the endothermic dehydrogenation reaction. In fluidized-bed reactors, the reaction mixture is intensively stirred, which lowers the reactor capacity and the selectivity of the reaction. The reactor and the regeneration unit are therefore fitted with horizontal grid plates, which considerably improves the process indices.

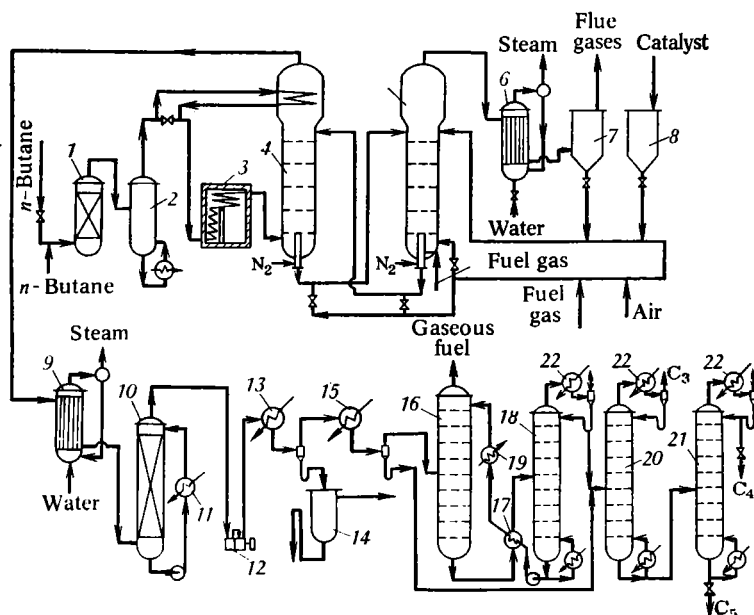


Fig. 7.12. Flow diagram of the first stage of dehydrogenation of paraffins:

1—drier; 2—vaporizer; 3—tubular furnace; 4—reactor; 5—regenerator; 6, 9—waste-heat boilers; 7—electric filter; 8—hopper; 10—scrubber; 11, 13, 15, 19—coolers; 12—compressor; 14—separator; 16—absorber; 17—heat exchanger; 18—stripping column; 20, 21—fractionating columns; 22—dephlegmators.

The technological process of dehydrogenation of paraffins to the corresponding olefins consists of three principal stages: (1) the dehydrogenation of the paraffin with regeneration of the catalyst; (2) the recovery of the butane-butylene (or pentane-amylene) fraction from the reaction products; (3) the separation of this fraction with recovery of butylenes (or isoamylenes). The flow diagram of the first two stages is given in Fig. 7.12 for the dehydrogenation of *n*-butane; it does not differ significantly from the flow diagram of the dehydrogenation of isobutane and isopentane.

Fresh and recycle *n*-butane in the liquid state are fed into drier 1 filled with an adsorbent (Al_2O_3 , molecular sieves) and then to vaporizer 2. The vapours formed are heated to 540-550 °C in tubular furnace

3 with a convective and a radiant section and pass into the space beneath the distribution grid of reactor 4 for dehydrogenation. The reactor is fitted with several grid plates, which divide the reaction volume into sections, thereby preventing the mixing and jet flow of the gases. The regenerated catalyst is led to the upper distribution grid and, hence, the fluidized catalyst bed and the reaction gases flow countercurrently, which creates the most favourable conditions for the process (the hotter catalyst is brought into contact with the partially reacted mixture and vice versa, as a result of which the reaction rates become equal throughout the entire volume). The upper part of the reactor is fitted with a "quench" coil, where the reaction gases are cooled by the *n*-butane being led to dehydrogenation. As a result, the temperature of the gases drops rapidly to 450-500 °C and their further decomposition is prevented. In the cyclones mounted on the top of the reactor the entrained catalyst is recovered from the gases and returned through the pipe into the catalyst bed. The heat of the gases formed during the dehydrogenation reaction is used in waste-heat boiler 9 for the generation of steam. They are then additionally cooled in scrubber 10 by the water circulating through cooler 11; the water entraps the catalyst dust that has passed through the cyclones.

The coked catalyst from the bottom of reactor 4 flows through a special pipe (a desorber), in which it is purged from the hydrocarbons by nitrogen. The catalyst is then entrapped by the stream of the hot gas (air + flue gases) and lifted by air to the top of the regeneration unit 5. The regeneration unit is also fitted with a distribution grid and several grid plates, which divide its volume into sections.

The regeneration is effected with the fluidized catalyst bed flowing countercurrently to the oxidizing gas fed to the lower distribution grid of the regeneration unit. Since it is necessary to avoid overheating, which deactivates the catalyst, the regeneration is carried out by using a mixture of air and flue gases containing only 2-3 percent (by volume) of oxygen. In this operation chromic oxide is partially oxidized to CrO_3 , which is reduced in the reactor with the formation of water, which has a detrimental effect on the properties of the catalyst. In order to avoid this, the flue gas is supplied to the desorber of the regeneration unit; this flue gas regenerates the catalyst, and nitrogen is introduced at a lower point to blow off the water vapours and the combustion gases. The regenerated catalyst is then entrapped at 640-650 °C by the transport gas and returned to the reactor.

The regeneration gases pass through the cyclones in the upper part of the regeneration unit and their heat is used in waste-heat boiler 6, where steam is generated. Then, the catalyst entrained by the gases is trapped in electric filter 7 and the flue gases are vented to the atmosphere. This catalyst is again returned by air to the regeneration unit. To make up the catalyst (its consumption is 0.5-1 percent

by weight), fresh catalyst flows from hopper 8 through a pipe and is entrapped by the gas and led to the dehydrogenation reactor.

The reaction gases leaving scrubber 10 have a temperature of 60-70 °C and the following approximate composition (in percent by weight):

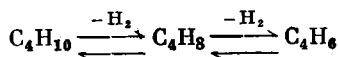
CH ₄ and H ₂	3	<i>n</i> -C ₄ H ₁₀	≈ 53
C ₂ H ₆ and C ₂ H ₄	2	1,3-Butadiene	2-3
C ₃ H ₈ and C ₃ H ₆	3-3.5	C ₅ and higher	2-2.5
<i>iso</i> -C ₄ H ₁₀	2-2.5	CO	1
<i>n</i> -C ₄ H ₈	31-32		

The reaction gases are compressed to 1.3 MPa in compressor 12 and cooled with water in cooler 13; the water is separated from the condensate in separator 14. The gas is then additionally cooled in brine cooler 15. The uncondensed gas, which consists of hydrogen, CO and lower hydrocarbons, passes into absorption column 16 refluxed by the C₅ fraction, which catches the vapours of the C₄ fraction and part of the vapours of the C₃ fraction from the gas. The still liquid of this column is run through heat exchanger 17 to fractionating column 18, in the still of which the C₅ fraction is accumulated and then sent through heat exchanger 17 and cooler 19 to reflux column 16. The light fraction of column 18, the hydrocarbon layer from separator 14 and the condensate from cooler 15 are subjected to fractionation in columns 20 and 21. The C₃ hydrocarbons are distilled off in the first column and the butane-butylene fraction is distilled off from the higher hydrocarbons in the second.

The final step of separation of the C₄ or C₅ fraction cannot be effected by simple fractionation because of the closeness of the boiling points of the components of the mixture. Extractive distillation is carried out using aqueous acetone, furfural, acetonitrile and *N*-methylpyrrolidone. The last two solvents are especially effective: in their presence the relative volatility of paraffins increases considerably as compared with olefins and dienes, and the paraffins can be distilled off as the head fraction and returned to the first stage of dehydrogenation. Then, the butylenes are distilled off together with butadiene from the solvent and are processed together with the C₄ fraction of the second stage of dehydrogenation. The recovered butylenes (or amylenes) pass to the second dehydrogenation stage.

One-Stage Dehydrogenation of Paraffins to Dienes. The above-described two-stage method of production of butadiene, which gives a relatively high yield (up to 65 percent), has a number of shortcomings: the gas mixtures must be separated after each stage and the power consumption and the capital cost are high. Much effort has therefore been devoted to the development of a single-step process for the conversion of *n*-butane and isopentane to butadiene and isoprene. This process is now operated industrially. The single-step pro-

cess involves two reversible consecutive dehydrogenation steps:



The equilibrium composition of this system depends on temperature and pressure. As can be seen from Fig. 7.13, as the temperature is raised the equilibrium concentration of *n*-butane decreases sharply, the content of *n*-butylenes passes through a maximum and the amount of butadiene increases but not to a considerable extent because of the simultaneous formation of hydrogen at both steps. These data show that the temperature chosen for the one-step process must be higher than that for the first step of the dehydrogenation of paraffins and the partial pressure of the reagents must be lower. Moreover, a catalyst is required to speed up appropriately the two dehydrogenation reactions (say, a chromia-alumina catalyst). Since with this catalyst steam cannot be used as the diluent, a new process has been developed, which proceeds at reduced pressure (0.015-0.02 MPa) and a temperature of 580-600 °C (this temperature is intermediate between the optimum temperatures for the first and second stages of paraffin dehydrogenation). Because of the use of vacuum reactors with a moving-bed catalyst have proved unsuitable for the single-step process. A strong deposition of coke and the frequent regeneration of the catalyst have been responsible for the use of the Houdry regenerative system.

The reaction unit for the one-step process (Fig. 7.14) incorporates a number of blocks consisting of 5-8 horizontal reactors with a fixed-bed catalyst. Each reactor operates batchwise according to the regenerative principle of heat utilization. During the coke-burning and catalyst-regeneration cycle the catalyst is heated up to 600 °C. This is followed by the evacuation of the combustion gases by applying a vacuum (1.5-2 min) and by the dehydrogenation reaction, in which the heat of the packing is used to carry out the endothermic reaction and the packing cools down to a permissible minimum temperature (580 °C). The reactor is then blown by superheated steam to remove the hydrocarbons (1.5-2 min) and the catalyst is again regenerated. In order to avoid too rapid cooling during the dehydro-

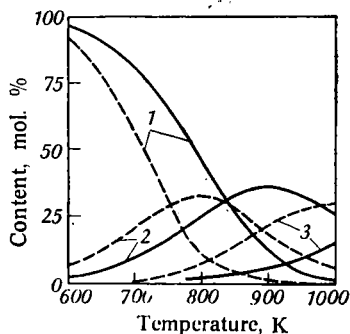


Fig. 7.13. Temperature dependence of the composition of the equilibrium mixture in the dehydrogenation of *n*-butane to *n*-butylene and butadiene (solid lines—at 0.1 MPa and dashed lines—at 0.01 MPa):

1—*n*-butane; 2—*n*-butylene; 3—butadiene.

generation period, granules of calcined alumina (a heat-retaining medium) are added to the catalyst. But in this case too the dehydrogenation and regeneration steps take only 5-9 min, the total duration of the operating cycle of the reactor being 15-20 min. The streams are switched automatically and a continuous and constant flow of the feedstock and reaction products is provided by the use of 5-8 reactors in each block.

The degree of conversion of the feedstock is 20-30 percent with a selectivity of ≈ 55 percent. The contact gas contains ≈ 11 percent

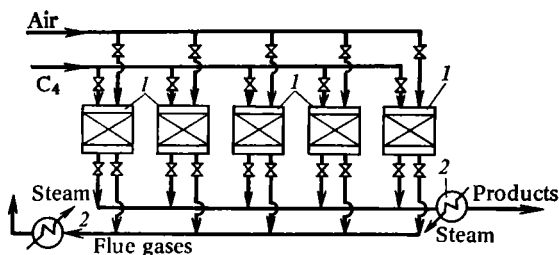


Fig. 7.14. Reaction unit for the one-stage dehydrogenation of paraffins to dienes: 1—reactors; 2—waste-heat boilers.

(by weight) of butadiene and 25-30 percent (by weight) of butylenes. Since the two dehydrogenation steps are effected under nonoptimum conditions the selectivity is lower than in the two-step process, but this is compensated by a reduction in the capital cost and power consumption owing to the omission of some operations.

7.3. Chemistry and Technology of Hydrogenation Processes

The processes of the hydrogenation of hydrocarbons and oxygen-containing and nitrogen compounds are extensively employed in the industry of basic organic and petrochemical synthesis mainly for the production of saturated hydrocarbons, ketones, carboxylic acids, alcohols and amines.

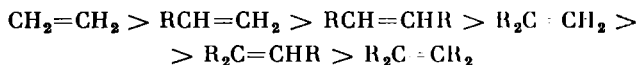
7.3.1. Hydrogenation of Hydrocarbons

7.3.1.1. Hydrogenation at the $C = C$ Bond

The hydrogenation of ethylene to ethane was first conducted in the middle of the 19th century by Faraday, who used platinum black as the catalyst. The catalysts used later for the hydrogenation of olefins were platinum, a spongy nickel catalyst (Raney nickel), supported

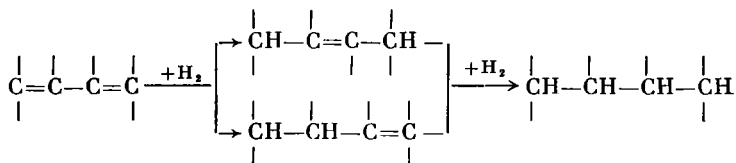
nickel, copper, mixed oxide catalysts (copper-chromite and zinc-chromite catalysts) and other heterogeneous catalysts. The catalysts most commonly used in industrial practice are metallic nickel and nickel supported on aluminium oxide, chromium oxide or other carriers. In their presence a high reaction rate is attained at 100–200 °C and a hydrogen pressure of 1–2 MPa. If the feedstock contains sulphur compounds, it is recommended that sulphur-resistant catalysts be used (nickel, tungsten and molybdenum sulphides) at 300–320 °C and 25–30 MPa.

The hydrogenation of hydrocarbons across the C=C bond proceeds very smoothly with an almost theoretical yield. The reactivity of olefins depends on the extent of replacement of carbon atoms at the double bond. Ethylene is hydrogenated most readily, and for its homologues the reaction rate decreases in the following order to the screening effect of the substituents:



Diene hydrocarbons with a straight chain are hydrogenated more readily than olefins. Depending on the structure of the diene, hydrogen can add first at the 1,4-position or simultaneously at the 1,4- and 1,2-positions; the reaction can often be stopped at this stage.

A more complete hydrogenation leads to paraffins:

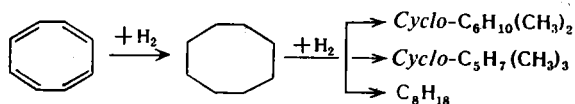


Polyene hydrocarbons are hydrogenated in an analogous way; they absorb two hydrogen atoms per each double bond until completely hydrogenated compounds are obtained. With an appropriate proportioning of hydrogen atoms and a suitable selective catalyst it is possible to carry out a partial hydrogenation of such compounds.

In cycloolefins the double bond can add hydrogen in the presence of the same hydrogenation catalysts. The presence of alkyl substituents at the double bond also lowers the reaction rate.

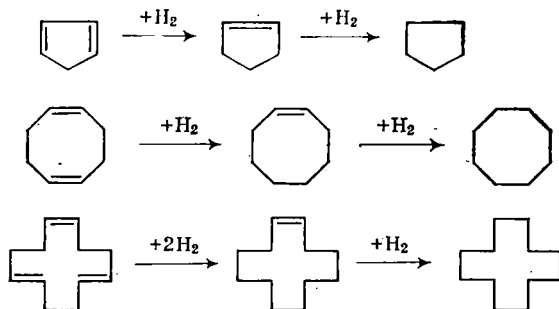
Safety measures must be observed in the hydrogenation of cycloolefins because of the possible development of the side hydrogenolysis reactions across the carbon-carbon bond; these reactions play a minor role in the hydrogenation of open-chain olefins. Under more severe conditions the ring is opened under the action of hydrogen, especially in the case of three- and four-membered cyclic systems. Hydrocarbons with six or more carbon atoms in the chain can iso-

merize under hydrogenation conditions to stable five- or six-membered rings:



These side reactions limit the choice of the temperature for the hydrogenation of olefins and especially cycloolefins, which must be taken into account in the determination of optimum process conditions.

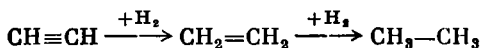
The hydrogenation of hydrocarbons at the C=C bond is extensively used for the stabilization of cracked gasoline, in the selective purification of liquid pyrolysis products from olefins, etc. In basic organic synthesis such hydrogenation reactions are employed for the production of some cycloolefins and cycloparaffins. Cyclopentene, cyclooctene and cyclododecene are new valuable monomers for synthetic rubber, and the corresponding cycloparaffins are used for the manufacture of dicarboxylic acids, cycloalkanones and lactams (page 415). The cycloolefins and cycloparaffins mentioned above are synthesized by the hydrogenation of cyclopentadiene (derived from pyrolysis products) and cyclic dimers and trimers of butadiene:



The hydrogenation to cycloparaffins can be carried out in the presence of heterogeneous catalysts (Ni and Co on supports), but in the case of the synthesis of cyclooctane and cyclododecane the best results have been obtained with homogeneous catalysts. Such catalysts are especially suitable for the selective hydrogenation of polyolefins to monoolefins—cyclopentene, cyclooctene and cyclododecene. The most frequently used catalyst is rhodium hydrocarbonyl with a tributylphosphine ligand, $\text{HRh}(\text{CO})_3 \cdot \text{P}(\text{C}_4\text{H}_9)_3$. In the presence of this catalyst at 140 °C and ≈ 2.5 MPa the degree of conversion of cyclododecatriene is close to 100 percent and the selectivity to the monoolefin is higher than 95 percent.

7.3.1.2. Hydrogenation at the C $\equiv$ C Bond

Acetylene and its homologues are hydrogenated at a slower rate than olefins, but the transiently formed olefins are easily displaced from the catalyst surface because of the lower sorbability and can therefore be obtained as the end products. The selective hydrogenation to olefins can be effected over supported platinum and palladium and also over cobalt and nickel molybdates, iron, etc. With a long contact time the hydrogenation proceeds to the paraffins:



Of the acetylene homologues, only those having a triple bond at the end of the chain react readily with hydrogen. Compounds with a triple bond in the middle of the chain are hydrogenated more slowly, and in this case the first and the second steps are separated more distinctly than with acetylene.

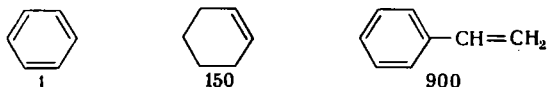
When nickel and especially copper are used and there is a hydrogen deficiency, acetylene gives other products, which are mixtures of its partially hydrogenated polymers. With a copper catalyst a solid polymeric compound, *cuprene*, is formed. It is used as a filler in the production of various materials.

In Germany, where there were no oil fields, the selective hydrogenation of acetylene was used for the industrial production of ethylene. The reaction was carried out at 180-320 °C with a 1.5- to 2-fold excess of hydrogen in the presence of a palladium catalyst on silicagel. An analogous process is operated today for the selective purification of ethylene from an acetylene impurity (acetylene is always formed in the pyrolytic processing of hydrocarbon gases, in which hydrogen is also liberated). Acetylene is removed by hydro-treating: the gas is passed through a contact vessel containing a catalyst (the catalysts recommended are supported nickel and nickel-cobalt-molybdates).

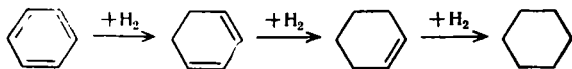
7.3.1.3. Hydrogenation of Aromatic Hydrocarbons

The catalysts used for the hydrogenation of aromatic systems are all Group VIII metals, but for industrial processes use is mainly made of nickel on supports, especially on Cr_2O_3 . With this catalyst a sufficient reaction rate is attained at 120-200 °C. In contrast to olefins, an increased pressure (1-5 MPa) is required, which is used not only to accelerate the reaction but also to increase the equilibrium degree of conversion, since the thermodynamics in this case is less favourable for hydrogenation. Aromatic hydrocarbons must be preliminarily purified from sulphur compounds, which are catalyst poisons.

The relative stability of an aromatic system is responsible for its lower reactivity on hydrogenation as compared with olefins. For example, the relative rates of the hydrogenation of benzene in the ring, a cycloolefin and of the double bonds in the side chain of an arylolefin are as follows (in arbitrary units):

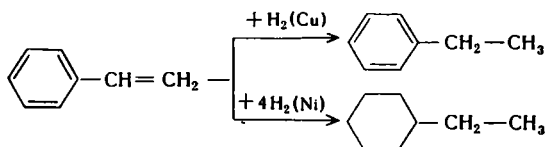


Because of this, even in spite of the consecutive-parallel type of reaction with a stepwise bond saturation

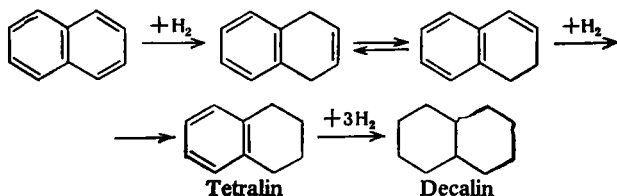


no cyclic olefins are detected in the reaction mass.

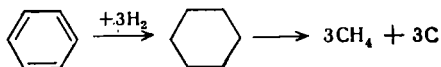
The homologues of benzene are hydrogenated at a slower rate than benzene, which is another manifestation of the deactivating effect of substituents at the bonds being hydrogenated. If an unsaturated side chain is present in an aromatic hydrocarbon, it is hydrogenated first. With a copper catalyst, which does not catalyze the hydrogenation of aromatic systems, only side chains are saturated; with nickel in the presence of an excess of hydrogen styrene, for example, is completely hydrogenated:



Aromatic hydrocarbons with condensed rings usually undergo stepwise hydrogenation with gradual saturation of bonds and rings. For example, the hydrogenation of naphthalene proceeds via the following steps (with the intermediate isomerization of α, α' -dehydronaphthalene to the more stable α, β -isomer):



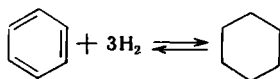
The conditions of the hydrogenation of aromatic hydrocarbons are mainly determined by the side reactions of hydrogenolysis with the cleavage of the side chains and rings. For instance, in the presence of a nickel catalyst at 290 °C benzene gives methane (up to 71 percent) and free carbon:



The side chains, especially longer chains, are cleaved even more readily. For example, the hydrogenation of *n*-propylbenzene may give not only propylcyclohexane but also ethyl- and methyl-substituted compounds, cyclohexane and lower paraffinic hydrocarbons. These side reactions determine the upper temperature limit upon hydrogenation of aromatic hydrocarbons.

The hydrogenation of aromatic hydrocarbons is employed on an industrial scale for the synthesis of a number of commercially important products, especially cyclohexane.

Cyclohexane, C_6H_{12} (a liquid; b.p. 80.7 °C) is contained in a small amount in the gasoline fractions of crude oils. The principal industrial method of its production is the hydrogenation of benzene:



If no thiophene impurity is present in benzene, the hydrogenation may be carried out over a supported nickel catalyst at 140–200 °C and 1–1.5 MPa. In the presence of sulphur compounds a suitable catalyst is one comprising nickel and tungsten oxides or sulphides, but higher temperature (320–360 °C) and pressures (≈ 30 MPa) are required for the process to be accomplished.

Cyclohexane has lately assumed significance for the production of cyclohexanone, caprolactam and adipic acid (page 415).

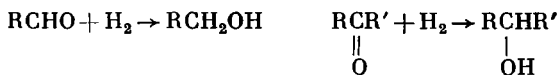
Tetralin and *decalin* obtained by the hydrogenation of naphthalene over a nickel catalyst in the gas and liquid phases, respectively, are valuable solvents.

7.3.2. Hydrogenation of Oxygen-Containing Compounds

Alcohols, aldehydes, ketones and carboxylic acids may contain unsaturated carbon-carbon bonds or aromatic systems capable of undergoing hydrogenation. In some cases it is necessary to hydrogenate selectively only these unsaturated bonds or aromatic systems, and in others, on the contrary, only oxygen-containing groups must be reduced. Here, it is important to find conditions that would be favourable for each of the processes indicated.

7.3.2.1. Hydrogenation of Aliphatic Aldehydes and Ketones

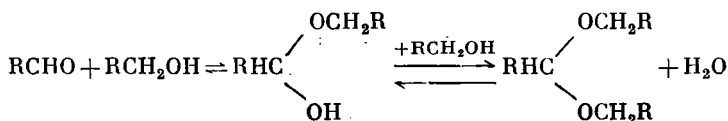
Saturated aldehydes and ketones are hydrogenated at the carbonyl group with the formation of primary or secondary alcohols:



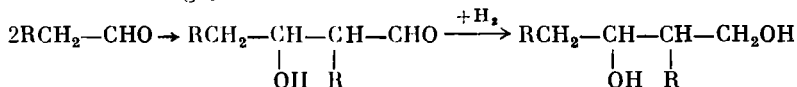
The catalysts most frequently used for these processes are supported nickel, copper and copper-chromite catalysts. If the feedstock contains sulphur compounds, mixed catalysts consisting of nickel, cobalt and tungsten oxides or sulphides may be used.

The aldehyde group is hydrogenated much more readily than the ketone group. The reduction of aldehydes can often be carried out under mild conditions—at 50–150 °C (with nickel or chromites) or at 200–250 °C (with metal sulphides); the hydrogenation of ketones requires more severe conditions—150–250 and 300–350 °C, respectively. In order to speed up the reaction and to increase the equilibrium degree of conversion, the process is carried out under pressure: the pressure is 1–2 MPa with a nickel catalyst, 5–20 MPa with chromites and up to 30 MPa with metal sulphides.

The alcohols formed in the hydrogenation of aldehydes give hemiacetals and acetals:



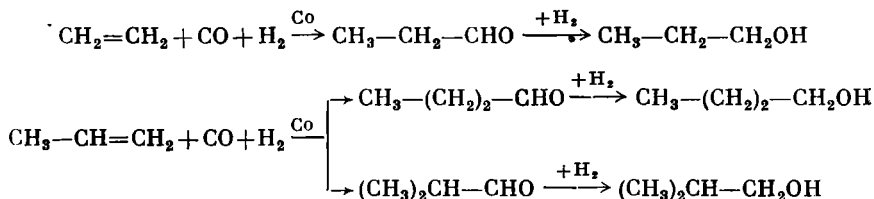
which are then reduced to alcohols with more difficulty than the aldehydes themselves. Therefore, when slightly active catalysts or low temperatures are used, acetals may be formed as by-products. Otherwise, they are also hydrogenated and are entirely converted to the same alcohols. Another side reaction that can occur at elevated hydrogenation temperatures consists of aldol condensation and the formation of glycols:



This reaction is suppressed by choosing a moderate temperature and by diluting the aldehyde, say with the alcohol formed. A decrease in the aldehyde concentration sharply lowers the rate of the aldol condensation because this reaction is second-order in the aldehyde.

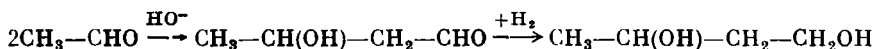
The hydrogenation of saturated aldehydes is of practical importance for the production of primary alcohols that cannot be obtained by more economical methods. This refers chiefly to *n*-propyl, *n*-butyl, isobutyl and some higher primary alcohols, when the hydro-

genation is the final step of the conversion of the aldehydes obtainable by Oxo synthesis from olefins, CO and H₂ to alcohols:

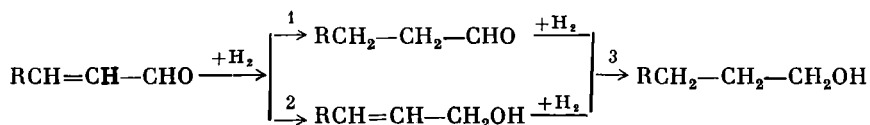


In some cases, the hydrogenation is carried out with the catalyst used for Oxo synthesis (cobalt), but in other schemes the reaction is effected over the catalysts mentioned above.

The hydrogenation of saturated hydroxyaldehydes and hydroxyketones is important for the synthesis of a number of glycols from the products of aldol condensation. For example, in the preparation of 1,3-butanediol, aldol is reduced in the presence of the catalysts mentioned above:

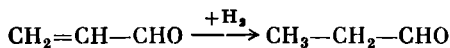


In the hydrogenation of unsaturated aldehydes and ketones the reaction may proceed in three directions: (1) the selective hydrogenation of an unsaturated carbon-carbon bond with the carbonyl group remaining intact; (2) the reduction of the carbonyl group with the unsaturated bond remaining unaffected; (3) the hydrogenation of all the functional groups and the formation of a saturated alcohol:



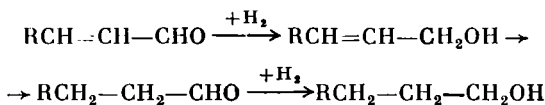
The selective hydrogenation of the double carbon-carbon bond with retention of the carbonyl group is easy to accomplish for ketones, whose functional group is less reactive than that in aldehydes. The catalysts used are platinum, nickel, copper and other metallic (but not oxide) catalysts. The process conditions do not significantly differ from those used for the hydrogenation of olefins, but in choosing the conditions one should take into account the possible side reduction of the ketone group. In the case of unsaturated aldehydes the hydrogenation of only the ethylenic linkage is a more complicated task. Milder conditions and catalysts that are relatively inactive with respect to the hydrogenation of carbonyl groups are required. It has been reported that with a copper catalyst in the presence of a limited amount of hydrogen even acrolein gives propionaldehyde

in a yield of 70 percent:

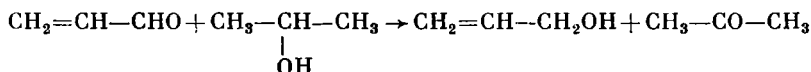


but the reaction is accompanied by the formation of saturated alcohols.

The reduction of unsaturated aldehydes and ketones to alcohols with the C—C bond remaining intact occurs preferentially over oxide catalysts capable of selectively reducing oxygen-containing compounds. Here, sufficiently mild conditions must be chosen in order to avoid side hydrogen-transfer reactions with the formation of saturated alcohols:

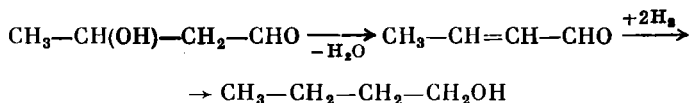


Because of the above-described difficulties, the reduction of acrolein to allyl alcohol in the chlorineless synthesis of glycerol is effected not by the action of hydrogen but by the catalytic hydrogen transfer between acrolein and isopropyl alcohol over $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$:

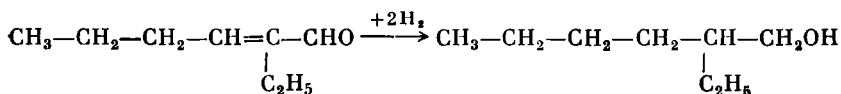


The hydrogenation of all the functional groups in unsaturated aldehydes or ketones with the formation of saturated alcohols is much easier to accomplish. The process is carried out either over metallic or oxide catalysts and under more severe conditions, which do not, however, allow the conversion of alcohols to hydrocarbons.

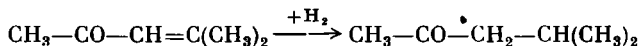
The hydrogenation of unsaturated aldehydes and ketones is employed commercially as the final step in the production of some higher alcohols and ketones. For example, the well-known method of synthesis of *n*-butyl alcohol from acetaldehyde involves the dehydration of aldol with the subsequent reduction of crotonaldehyde:



Analogously, *n*-butyraldehyde gives 2-ethylhexyl alcohol, an important intermediate in the manufacture of plasticizers—the esters of dicarboxylic acids:

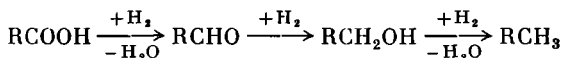


Isobutyl methyl ketone, which is an excellent solvent and an extractant, is produced in a similar way from acetone via mesityl oxide:



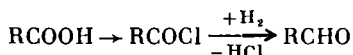
7.3.2.2. Hydrogenation of Aliphatic Carboxylic Acids and Esters

The reduction of the carboxyl group proceeds successively through the steps of formation of aldehydes, alcohols and hydrocarbons:

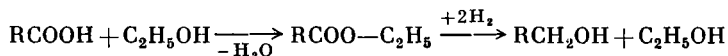


The process can be stopped only at the alcohol step; further hydrogenation of alcohols is undesirable.

Aldehydes are reduced much faster than acids, which is why the final products do not contain even traces of aldehydes. The production of aldehydes from acids can be accomplished indirectly—via acid chlorides which are reduced by hydrogen over a platinum or palladium catalyst:



The products of the reduction of carboxylic acids are primary alcohols. The acids, however, react with more difficulty than their esters, which is why the alcohols are often obtained by the hydrogenation of the esters. This results in the formation of alcohols having the same number of carbon atoms as the starting acid, and the alcohol used for the synthesis of an ester is recovered:



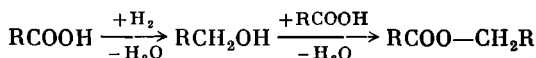
Metallic hydrogenation catalysts are not effective for the reduction of the carboxyl group and the success of the process has been made possible by the development of active catalysts of the oxide type, which have a selective adsorptive capacity with respect to oxygen-containing compounds. The catalysts that are most frequently used in industrial practice are copper- and zinc-chromite catalysts ($\text{CuO} \cdot \text{Cr}_2\text{O}_3$ and $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$) and also copper-zinc-chromite catalysts ($\text{CuO} \cdot \text{ZnO} \cdot \text{Cr}_2\text{O}_3$). The reaction is carried out at 250–350 °C and a high pressure (25–35 MPa), which is required to increase the reaction rate and the equilibrium degree of conversion.

The reduction of esters involves their alcoholysis by the alcohol formed:



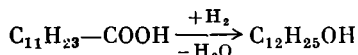
and if the hydrogenation is not brought to completion, the newly formed esters are by-products. Usually, the by-products are the hydrocarbons that are formed as a result of a more complete reduction.

When the carboxylic acids themselves are hydrogenated, the alcohols formed react with them to give esters:

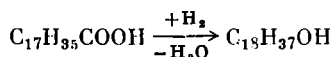


and the hydrogenation process is gradually facilitated. This permits the addition of only a small amount of an ester (or an alcohol) or even the direct hydrogenation of carboxylic acids. In practice, such a process is advantageous because there is no need for a special step leading to the formation of esters and the recovery of alcohols.

The hydrogenation of the esters of saturated monobasic acids gives the corresponding alcohols in a yield of 90-95 percent. This route is employed industrially for the production of higher primary alcohols with a straight carbon chain, say lauryl alcohol from the ester of lauric acid:

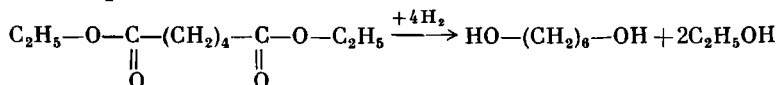


or octadecyl alcohol from the ester of stearic acid:



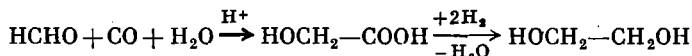
The hydrogenation of synthetic fatty acids obtained by the oxidation of paraffins have assumed great commercial importance. These acids also have a straight carbon chain and give on hydrogenation alcohols of a normal structure. Here, the fraction of C_{10} - C_{18} acids yields a mixture of primary alcohols, which, like lauryl and hexadecyl alcohols, is suitable for the production of high-quality surfactants of the alkyl sulphate type and also of nonionic detergents based on ethylene oxide. The hydrogenation of the fraction of C_7 - C_9 acids results in the formation of a mixture of alcohols, which is successfully used for the synthesis of plasticizers, assistants in the textile industry, and flotation agents

The esters of saturated dibasic acids when hydrogenated under the same conditions form glycols. The process occurs sufficiently smoothly only for acids that have at least two methylene groups. This method is employed for the production of 1,6-hexanediol from the ester of adipic acid:

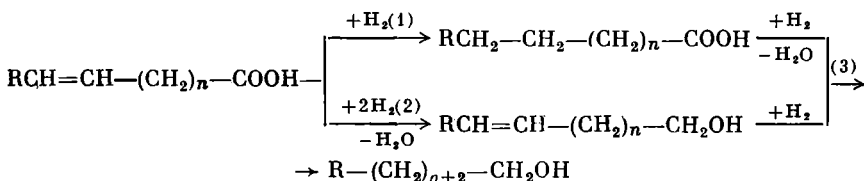


1,6-Hexanediol is used for the production of polyesters.

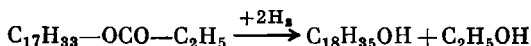
Glycolic acid when subjected to hydrogenation is converted to ethylene glycol; this reaction forms the basis of the industrial synthesis of ethylene glycol from formaldehyde, carbon monoxide and water:



Unsaturated carboxylic acids and their esters can be hydrogenated in three directions: (1) across the ethylenic bond with retention of the carboxyl group (the preparation of saturated acids); (2) across the carboxyl group with retention of the double bond (the preparation of unsaturated alcohols); (3) across both functional groups with the formation of saturated alcohols:



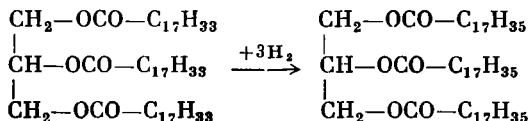
The reduction of the carboxyl group with retention of double bonds is accomplished in the same way as for saturated acids—the acids or their esters are hydrogenated over selective catalysts. The best catalyst is a zinc-chromite catalyst ($\text{ZnO} \cdot \text{Cr}_2\text{O}_3$). This route is used to produce unsaturated oleyl alcohol from ethyl oleate:



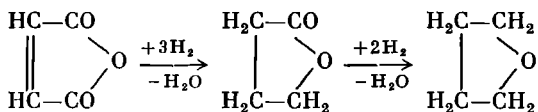
Of greater commercial significance is the hydrogenation of unsaturated fatty acids and their esters across the ethylenic bonds leading to saturated acids. The best catalyst for this process is reduced nickel used in a finely divided state or on a support (this catalyst is active at 125–200 °C). The esters react at a faster rate than the unsaturated acids themselves; the reaction rate decreases with lengthening and branching of the chain. Here, the double bond in acids is less reactive than in olefins, which is an indication of the deactivating effect of the carboxyl group.

The commercial importance of this process is due to the conversion of relatively invaluable unsaturated fats and oils, which are liquid at ordinary temperature, to solid saturated fats. The process is therefore called the hardening of fats or their hydrogenation. Liquid fats and oils (cottonseed oil, corn oil, soybean oil, linseed oil, fish oil, etc.) are mixtures of esters known as the glycerides of unsaturated acids (oleic, eleostearic, erucic and other acids). Upon their hydrogenation over a nickel catalyst the double bonds are saturated and

a solid fat is formed, which has a low iodine number:



A process that has lately become of increasing importance in industrial practice is the hydrogenation of maleic anhydride to γ -butyrolactone and tetrahydrofuran:

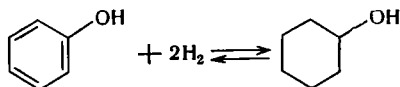


The reaction is effected over a nickel catalyst in the gas or liquid phase; the relative yield of γ -butyrolactone and tetrahydrofuran can be varied over wide limits. The first compound is used for the synthesis of pyrrolidones and the second as a solvent.

7.3.2.3. Hydrogenation of Aromatic Oxygen-Containing Compounds

The hydrogenation of phenols, aromatic aldehydes, ketones and carboxylic acids may proceed in two main directions: (1) with the saturation of the aromatic system and with the formation of cyclohexane derivatives; or (2) with the reduction of the oxygen group. These reactions have some specific features as compared with the hydrogenation of aliphatic compounds.

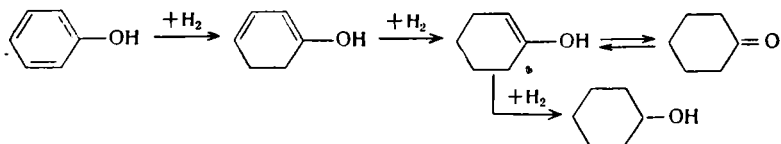
Phenol when hydrogenated over a nickel catalyst (130–150 °C and 0.5–2 MPa) gives *cyclohexanol*, $\text{C}_6\text{H}_{11}\text{OH}$ (a liquid; b.p. 160 °C):



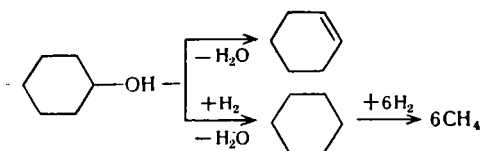
This is an important intermediate for the synthesis of cyclohexanone, adipic acid and caprolactam. The production of these compounds from benzene via cyclohexane has already been described. The reaction was first accomplished with phenol as the feedstock, and this route is still used today. Cyclohexanol is also employed as a solvent for polymers, oils and fats.

One of the by-products in the production of cyclohexanol from phenol is cyclohexanone, the yield of which increases with increasing temperature and decreasing pressure. Its formation can be accounted for by the reaction of equilibrium dehydrogenation of cyclohexanol, but it is more likely that the process occurs in a stepwise manner via the enol form of cyclohexanone, which is then isomerized to the

keto form or is hydrated further to an alcohol:

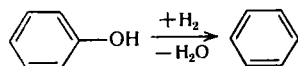


The other by-products of phenol hydrogenation are cyclohexene (due to the dehydration of cyclohexanol), cyclohexane and methane:



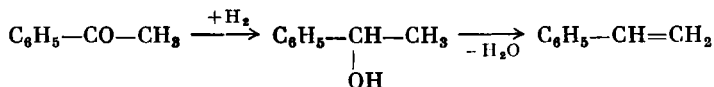
The homologues of phenol and polyhydric phenols are capable of undergoing hydrogenation in the aromatic ring under similar conditions.

Besides, phenols can be selectively hydrogenated to hydrocarbons with retention of the system of aromatic bonds:

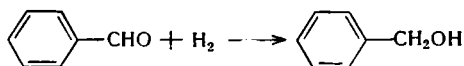


The last reaction proceeds more difficultly than the reduction of the alcoholic group. It is important for the dephenolization of the products of the destructive hydrogenation of various gums formed during the pyrogenetic processing of solid fuels.

In contrast to aliphatic alcohols, aromatic alcohols are sufficiently readily reduced to hydrocarbons. The reduction of fatty-aromatic ketones to the corresponding alcohols should therefore be carried out under as mild conditions as possible. For example, in one of the oxidative methods of preparation of styrene from ethylbenzene the hydrogenation of acetophenone to α -phenylethyl alcohol is effected in the presence of a copper-iron-chromite catalyst:

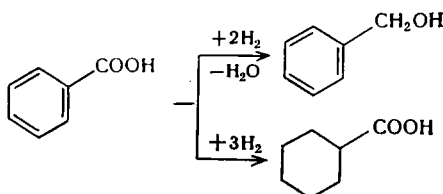


The hydrogenation of aromatic aldehydes may be limited to the formation of an alcohol, since aldehydes and ketones differ sufficiently strongly in their ability to undergo reduction:



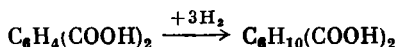
Attempts to hydrogenate aromatic aldehydes, ketones and alcohols only across the aromatic bonds with retention of the oxygen functional groups have failed: the alcoholic or carbonyl group has to be protected by using the derivatives of these compounds (esters, acetals).

Aromatic carboxylic acids can be hydrogenated with reduction of the carboxyl group or with saturation of the aromatic system:



The first reaction is analogous to the reduction of aliphatic acids and their esters and proceeds over the same catalysts. The hydrogenation with saturation of the aromatic system is in many respects similar to the hydrogenation of the corresponding hydrocarbons (over a nickel catalyst at 160-200 °C and under hydrogen pressure). The aromatic ring of carboxylic acids is hydrogenated much more difficultly than that of benzene or phenol.

All the three isomeric phthalic acids are converted upon hydrogenation to the corresponding hexahydrophthalic acids, which are of some value for the production of polyesters:



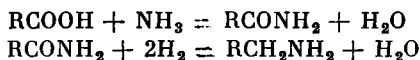
The hydrogenation of benzoic acid is accomplished industrially as one of the steps of the synthesis of caprolactam from toluene (page 609).

7.3.3. Hydrogenation of Nitrogen Compounds

In the industry of basic organic and petrochemical synthesis the hydrogenation of nitrogen-containing compounds (the amides of acids, nitriles, nitro compounds, etc.) is carried out mainly for the production of amines, which are extensively used in the synthesis of polyamides, isocyanates, carbamates, polyurethanes, etc.

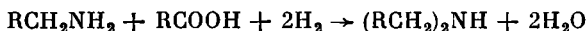
7.3.3.1. Hydroammonolysis of Carboxylic Acids and Carbonyl Compounds

The *hydroammonolysis of carboxylic acids* is based on two reactions—the formation of acid amides under the action of ammonia and the hydrogenation of amides to amines:



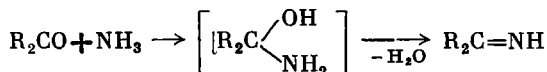
The first reaction, which has already been described (see Chapter 3), proceeds at elevated temperature without catalysts. The reduction of amides to amines occurs in the presence of catalysts (hydrogenation catalysts)—nickel (at 250 °C and 1-2 MPa), nickel, tungsten and molybdenum sulphides (at 300-330 °C and ≈ 20 MPa), etc. When the process is accomplished commercially, there is no need for the recovery of amides, and the two reactions are effected jointly. As a result, a primary amine is obtained with the same number of carbon atoms as in the starting carboxylic acid.

As the amine is formed it can react with the carboxylic acid and the resultant substituted amide is reduced by hydrogen to a secondary amine:



If the end product is a primary amine, this reaction must be suppressed, which requires the presence of a large excess of ammonia—a nearly 10-fold excess with respect to the required theoretical amount. The excess ammonia is recovered from the reaction mixture and circulated in the system, just as in the synthesis of amines from ammonia and alcohols considered earlier.

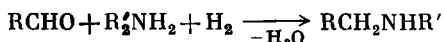
The *hydroammonolysis of aldehydes and ketones* is also based on a combination of two reactions—the condensation of carbonyl compounds with ammonia and the hydrogenation of the products formed. The first reaction gives aldimines (or ketimines):



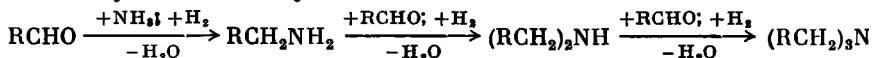
Their hydrogenation leads to amines with the same number of carbon atoms as in the starting carbonyl compound:



When the two reactions are combined, the aldehydes give amines, in which the amino group is at the primary carbon atom, and ketones give amines with the amino group at the secondary carbon atom. If primary or secondary amines are taken instead of ammonia, secondary or tertiary amines are obtained:



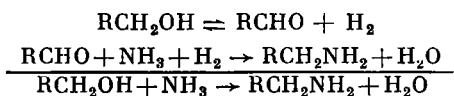
Evidently, in the interaction of the carbonyl compounds with ammonia and hydrogen as the initially formed primary amine is accumulated in the reaction mass it participates to an increasing extent in the hydroammonolysis process according to the reactions given above. As a result, a system of consecutive-parallel reactions takes place, which leads to the formation of a mixture of primary, secondary and tertiary amines:



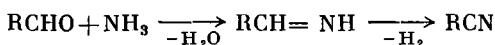
The composition of the resultant mixture of products depends on the molar ratio of ammonia to the carbonyl compound in the starting mixture. A good yield of the primary amine can be achieved by using an almost 10-fold excess of ammonia circulating in the system.

The interaction of ammonia with carbonyl compounds does not require special catalysts, and hydroammonolysis should be carried out only with hydrogenation-type catalysts. The catalysts proposed for the process are nickel (80-150 °C and 0.2-2 MPa) and a mixture of nickel and tungsten sulphides (300-320 °C and ≈ 20 MPa).

The hydroammonolysis reaction is of importance for the synthesis of amines from alcohols. It is commonly carried out with an acid-type catalyst (Al_2O_3 , aluminosilicates, etc.), just as the N-alkylation (page 293). The dehydrogenation catalysts (Ni, Cu, Co) are also suited for this purpose; in their presence the reaction proceeds via the intermediate step of dehydrogenation of an alcohol to an aldehyde (or a ketone) with the subsequent hydroammonolysis of the latter to an amine:



If the process is carried out without addition of hydrogen, the major proportion of the transiently formed aldimine will undergo dehydrogenation to a nitrile:



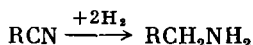
The process is therefore effected with a mixture of the vapours of alcohol, ammonia and hydrogen. Depending on the molar alcohol-ammonia ratio, mixtures of differing composition are obtained; this process is kinetically more favourable for the formation of a primary amine than the alkylation of ammonia by alcohols. The synthesis of amines from alcohols and ammonia in the presence of hydrogen over dehydrogenation-hydrogenation catalysts is carried out in the gas phase at 200-250 °C and 1-2 MPa. The conditions indicated are milder than those used for the alkylation of ammonia by alcohols and the process is not accompanied by the formation of by-product olefins. On the account of this, it may be more preferential for the synthesis of amines, especially from higher and secondary alcohols.

7.3.3.2. Hydrogenation of Nitriles

The hydrogenation of nitriles is a convenient route of synthesis of amines. It has become industrially important for those cases, where nitriles are cheaper and more available than chloro derivatives or alcohols with the same number of carbon atoms.

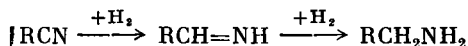
Various nitriles, beginning with hydrocyanic acid, add hydrogen in the presence of typical hydrogenation catalysts (Ni, Co, Cu) under

pressure:

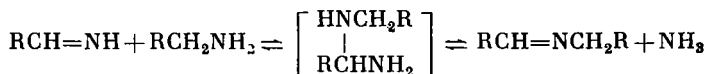


The reaction is, however, not simple since secondary and tertiary amines are formed as by-products, and secondary amines may become the dominant product. It has been found that in the presence of excess ammonia a primary amine is formed as the major product in a yield of 80-90 percent.

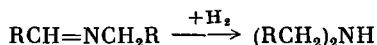
The formation of by-products and the effect of excess ammonia are accounted for by the intermediate formation of aldimines:



They can react with the amine present in the reaction mass according to the following reversible reaction (a hypothetical diamine with amino groups at the same carbon atom must immediately break down with the liberation of ammonia):

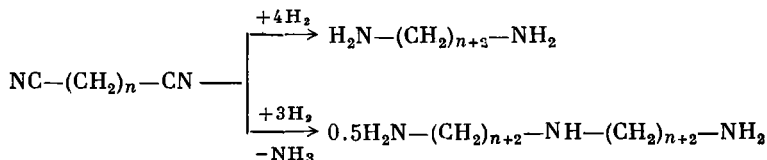


The resultant N-substituted aldimine gives upon hydrogenation a secondary amine:

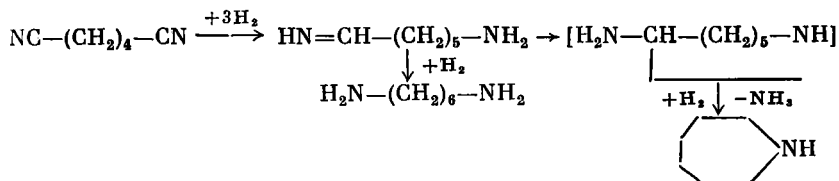


A tertiary amine is formed in the same way. In the presence of an excess of ammonia the equilibrium of the above reaction is shifted to the left and the formation of secondary amines is suppressed.

The by-product formed in the hydrogenation of dinitriles is a linear triamine with one secondary amino group:



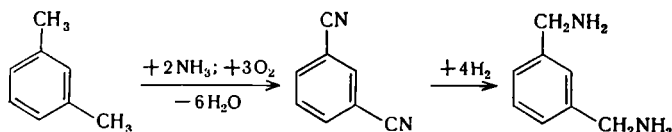
Besides, with a sufficient number of carbon atoms between the nitrile groups there may take place a ring closure with the formation of cyclic amines, say hexamethyleneimine from adipodinitrile:



Of the products of the hydrogenation of nitriles, *hexamethylenediamine*, $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ (a solid; m.p. 42°C) is of prime practical importance. It is obtained by the hydrogenation of adiponitrile and used as one of the starting compounds in the production of the synthetic fibre nylon (the equivalent term used in this country is anid) and also of hexamethylene diisocyanate and polyurethanes.

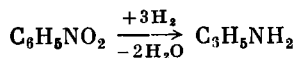
The suitable catalysts for the hydrogenation of adiponitrile are a cobalt-copper catalyst (at 125°C and 20-30 MPa), cobalt on silica-gel, and others. Good results are given by Raney nickel or a cobalt catalyst at $80-100^\circ\text{C}$ and 5-8 MPa. In all cases the reaction occurs in the liquid phase in the presence of an excess of ammonia; the yield of hexamethylenediamine is 80-90 percent.

m-Xylylenediamine has become important for the production of polyamides; the polycondensation of *m*-xylylenediamine with adipic acid gives a polymer which is capable of forming a fibre of the nylon type. *m*-Xylylenediamine is synthesized from *m*-xylene by way of its oxidative ammonolysis to dinitrile with subsequent hydrogenation:

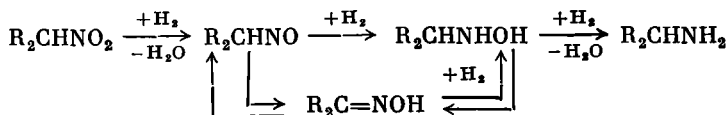


7.3.3.3. Hydrogenation of Nitro Compounds

The reduction of nitro compounds to amines discovered by N.N. Zinin in 1842 was the first process of this type accomplished industrially for the production of aniline:

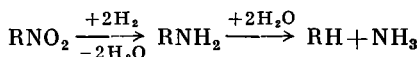


Aromatic nitro compounds are reduced industrially by using various agents (iron with hydrochloric acid, metal sulphides, zinc or iron with a strong alkali), by electrolytic reduction and, finally, by catalytic hydrogenation. The reaction proceeds via a series of intermediate steps, which include, with most of the reducing agents mentioned, the intermediate formation of nitroso compounds and hydroxylamines. Aliphatic nitroso compounds are isomeric to oximes, which can also be formed as intermediates during the reduction:

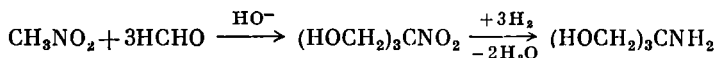


The only method employed in the industry of basic organic and petrochemical synthesis for the reduction of nitro compounds is the catalytic hydrogenation with the aid of hydrogen. This method becomes increasingly important owing to the low cost of hydrogen, the possibility of large-tonnage continuous production and other advantages.

In carrying out the catalytic hydrogenation of any nitro compound one should take into account that under more severe conditions the C—N bond can be cleaved with the liberation of NH_3 :

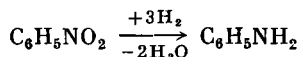


The *hydrogenation of aliphatic nitro compounds* to amines is most often effected with a nickel catalyst at 150–200 °C and 1–5 MPa. This method of production of aliphatic amines has found industrial application as a result of the realization of the direct synthesis of nitroparaffins by the nitration of paraffins. It has also become important for the production of amino-alcohols from the products of the condensation of nitro compounds with formaldehyde; an example is the following reaction:



The *reduction of aromatic nitro compounds* to amines may be accompanied by the hydrogenation of the aromatic ring, which is especially typical when the reaction is catalyzed by platinum, palladium and nickel. It is for this reason that use is most often made of copper (at 200–300 °C and 0.15–0.2 MPa). If the feedstock contains catalyst poisons, the hydrogenation is effected using nickel and molybdenum sulphides at 300–350 °C and 20–30 MPa. Copper-chromite catalysts are also recommended for this purpose.

Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, is produced by the catalytic hydrogenation of nitrobenzene in the presence of a copper catalyst in the gas phase:

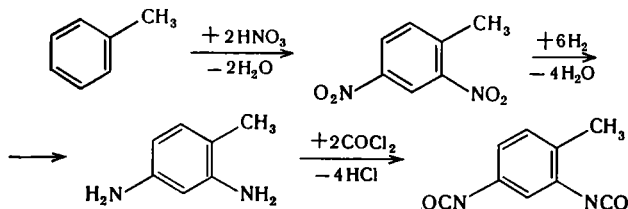


Aniline is used as the feedstock for the production of cyclohexylamine and caprolactam (page 602), phenyl isocyanate and the well-known pesticide isopropyl phenylcarbamate (IPC), $\text{C}_6\text{H}_5\text{—NHCOO—CH}(\text{CH}_3)_2$.

Pesticides are also synthesized by using *m*-chloroaniline, which is obtained by the reduction of *m*-chloronitrobenzene, and naphthylamines and other aromatic monoamines.

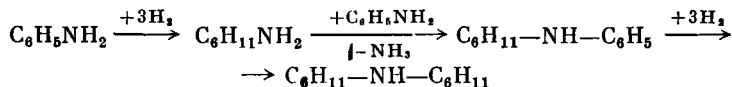
Aromatic di- and polyamines are commercially important for the manufacture of polymeric materials. *m*-Phenylenediamine, which is produced by the hydrogenation of *m*-dinitrobenzene, is used for

the synthesis of polyamides by way of polycondensation with aromatic dicarboxylic acids. Toluylenediamine formed in the hydrogenation of 2,4-dinitrotoluene is an intermediate in the synthesis of toluylene diisocyanate:



which is used as the basic monomer in the production of polyurethanes and polyester urethanes.

The *hydrogenation of aromatic amines in the ring* is carried out for the synthesis of cyclohexylamine, which is an intermediate in one of the methods of caprolactam production. The nuclear hydrogenation of aniline involves side reactions—the splitting-off of the amino group and the condensation of cyclohexylamine with aniline with the subsequent hydrogenation leading to the formation of a secondary amine (dicyclohexylamine):



The formation of dicyclohexylamine can be reduced by lowering the concentration of amines in the reaction mass (by carrying out the reaction in solutions or by using an excess of hydrogen) and by choosing a suitable catalyst. According to the available data, the best catalysts are cobalt oxide activated by lime and supported nickel.

7.3.4. Technology of Liquid-Phase Hydrogenation

Liquid-phase hydrogenation is effected by bubbling hydrogen through the liquid reaction mass. This method is always used for the hydrogenation of a high-boiling compound (fats, higher carboxylic acids and their esters, dinitriles, dinitro compounds) since the conversion of these compounds to the saturated vapour state would require a large excess of hydrogen and the expenditure of extra money. However, more volatile compounds can also be hydrogenated at a high pressure in the liquid phase.

The processes of liquid-phase hydrogenation are classified as follows.

According to the composition of the liquid phase they may be divided into the following groups:

1. The hydrogenation in the medium of the compound being hydrogenated without addition of foreign agents. In this case, the liquid reaction mass consists of the starting organic compound, in which the products formed are gradually accumulated. This method is the most favoured one.

2. The hydrogenation in a solution of substances which are inert under the reaction conditions. This method is used for the reduction of compounds which are solid at the reaction temperature (the production of sorbitol and mannitol from carbohydrates in aqueous solution, the hydrogenation of polymers) or are liable (at their high concentration) to form a large amount of by-products. For example, aldehydes are hydrogenated in the form of their solutions in the corresponding alcohols in order to avoid the development of aldol condensation processes.

3. The hydrogenation in emulsions, say the reduction of aromatic dinitro compounds in a water emulsion. In this process, the conditions of the removal of the reaction heat are improved, the recovery of the water-soluble diamine is facilitated and the decomposition of thermally unstable dinitro compounds is prevented.

Depending on the form in which the catalyst is used, liquid-phase hydrogenation processes may be divided into three groups:

1. With a finely dispersed catalyst, which is often obtained directly in the mass of the compound being hydrogenated (the decomposition of metal formates or carbonyls). Such a catalyst is very active but is difficult to separate from the hydrogenation product upon subsequent processing.

2. With a catalyst ground to a certain particle size and suspended in the reaction mass. The catalyst is more easily separated from the hydrogenation product upon subsequent filtration, but it gradually undergoes attrition during the operation, which leads to the wear of the walls of the vessels and pipes.

3. With a fixed catalyst used in the form of granules of various shapes, which are sufficiently large and are not carried away by the liquid and gas streams. This variant is most suitable because the need for the subsequent filtration of the hydrogenation product is eliminated.

Finally, liquid-phase hydrogenation can be operated either batch-wise or continuously.

Types of Reaction Vessels. The reaction mass in liquid-phase hydrogenations is, as a rule, a three-phase system (a liquid reagent, a solid catalyst and gaseous hydrogen). The reaction occurs on the catalyst surface, its velocity being dependent, other conditions being equal, on the hydrogen concentration in the liquid, on the rate of its dissolution in the reaction mass and the rate of diffusion of hydrogen to the catalyst surface. The increase of the reaction rate is favoured by high hydrogen pressure and the stirring of the reaction

mass, which is characteristic of all hydrogenation processes.

The type of reaction unit employed for liquid-phase hydrogenation depends on the exothermicity of the reaction and the method used to remove the heat. Only in rare cases is the amount of heat evolved so small that the reaction can be accomplished without cooling (the hydrogenation of carboxylic acids and their esters). When volatile compounds are to be hydrogenated (the conversion of benzene to cyclohexane), the heat is removed by the evaporation of the components of the mixture, which are condensed and returned to the reactor. For processes that make use of dispersed or suspended

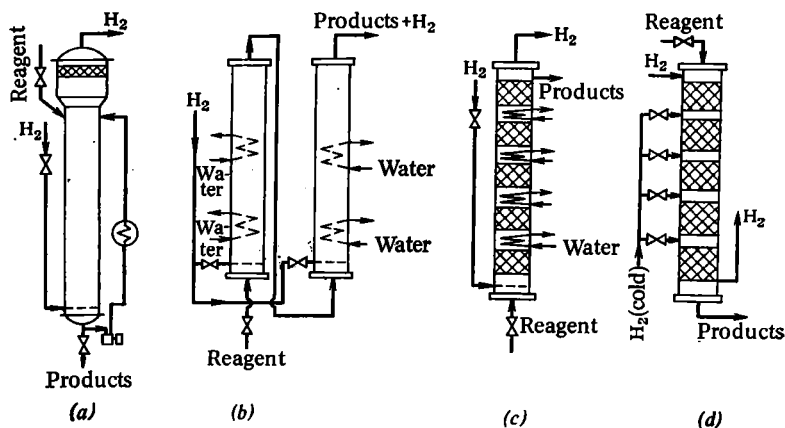


Fig. 7.15. Reaction units for liquid-phase hydrogenation:

a—batch column with an external cooler for the process carried out over a suspended catalyst; b—cascade of continuous reactors with an internal cooler for the process carried out over a suspended catalyst; c—continuous reactor with an internal cooler for the process carried out over a fixed catalyst bed; d—continuous reactor cooled by cold hydrogen for the process carried out over a fixed catalyst bed.

catalysts forced cooling with the aid of internal or external coolers is most often effected, when the heat of the reaction is used at a suitable temperature for the generation of steam. The removal of heat is more difficult in processes that employ a fixed catalyst; in such cases, the mixture is cooled in a stepwise manner.

Figure 7.15a shows a batch reactor carrying a suspended catalyst. The reaction column designed for an appropriate pressure is filled by three-fourths with the liquid reaction mass, through which hydrogen (fed at the bottom through the distribution grid) is bubbled. The widened upper part of the column serves as a spray trap (it has trays or a layer of packing consisting of Raschig rings). The reaction heat is removed by way of forced circulation of the liquid through an external cooler. The hydrogen is fed to the column in large excess in order to agitate the motion of the liquid and to maintain the

catalyst in the suspended state. The unreacted hydrogen leaves the column at the top and usually entrains the vapours of the reagents and water (water is liberated upon hydrogenation). It is cooled, separated from the condensate and returned by a circulation compressor to the hydrogenation column. When the operation is completed, the reactor is filled with a fresh portion of the reagent with the catalyst, the liquid is heated by steam to the required temperature and the circulation of hydrogen is started. The completion of the process is indicated by the data obtained by the analysis of the reaction mass.

The reactor just described is not suitable for the continuous process, since it operates in the back-mix regime. With a continuous supply of the reagents and continuous removal of the product formed the capacity of the reactor and the extent of reaction will be unsatisfactory.

It is for this reason that for the continuous process employing a suspended catalyst use has to be made of a cascade of two or more successive columns (Fig. 7.15*b*). In this scheme, the reagent is fed only to the first column and the liquid overflows from one column to another. In order to avoid excessive stirring of the reaction mass, the best way is to employ internal cooling and the direct concurrent flow of the liquid and the gas fed to the lower part of the columns and withdrawn at the top. Depending on the operating temperature, either water or the water condensate may serve as a cooling agent. In the latter case, steam is generated in the plant and used for process needs.

When a fixed catalyst bed is employed, only in rare cases of weakly exothermic reactions may adiabatic reactors with a single continuous catalyst bed be used. The catalyst is most often packed into special perforated-bottom cases; placed between the cases are cooling oils (Fig. 7.15*c*) or cold hydrogen is introduced (Fig. 7.15*d*), which accumulates the reaction heat. In such cases, each catalyst bed operates under adiabatic conditions and the reagents while passing through it are warmed up; the mixture cools down before it enters the next catalyst bed. The liquid and hydrogen streams may, in principle, move in three directions: the countercurrent flow of the descending liquid and the ascending gas; the concurrent upward flow of the liquid and the gas; the concurrent downward flow of the liquid and the gas. In the second case, which is shown in Fig. 7.15*c*, the reactor operates with the catalyst bed being submerged, which leads to a considerable increase in its hydraulic resistance. If both reagents are fed at the top of the column, the catalyst packing is only refluxed by the liquid (Fig. 7.15*d*) and the hydraulic resistance becomes low.

Liquid-phase hydrogenation has lately been carried out by using a combination of two reactors with a suspended and a fixed catalyst.

(Fig. 7.16). The major part of the reaction is effected in the first reactor and the heat is removed by one of the methods described above. In the second reactor, only a small fraction of conversions occur, and cooling is not required at all. The reactor capacity and the degree of conversion of the raw material are high owing to the combination of reactors, the designs of which are close to the back-mix and plug-flow models, respectively.

In a number of cases, the hydrogenation columns may be constructed of ordinary steel. If the process is accomplished at a high pressure, which favours hydrogen corrosion, or involves corrosive substances (carboxylic acids, etc.), special grades of steel are required or the steel body of the reactor must be faced with an alloyed steel or other corrosion-resistant metals.

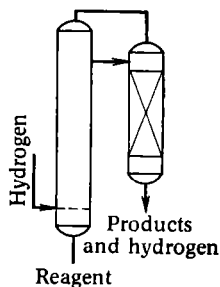


Fig. 7.16. A system of two reactors with a suspended and a fixed catalyst for liquid-phase hydrogenation.

Flow Diagram of Liquid-Phase Hydrogenation. The flow diagrams of the majority of liquid-phase hydrogenation processes have many features in common, this being due to the application of a high pressure, an excess of

recycle hydrogen and a heterogeneous catalyst. They differ only in the type of the catalyst (a suspended or a fixed catalyst) and also in the method used for the separation of the products, which depends on their physical properties.

As a typical example of flow diagrams used for the liquid-phase hydrogenation process with a suspended catalyst, let us consider the flow diagram of the production of higher fatty C_{10} - C_{18} alcohols from methyl or other esters of synthetic fatty acids obtained by the oxidation of paraffins (Fig. 7.17). The reaction is carried out at ≈ 30 MPa and 300°C over a copper-chromite catalyst containing barium oxide (the Adkins catalyst). The low heat effect of the process permits the use of adiabatic reactors with preheating of the reagents to the required temperature.

Fresh and recycle hydrogen is compressed by compressors 1 and 2 to 30 MPa, mixed and heated in heat exchanger 3 (by the hot reaction gases) and in tubular furnace 4 (by the flue gases). The ready ester is fed by pump 5 through steam heater 6 into the reactor and the catalyst (as a suspension in higher alcohols) is fed by pump 16. All the components are mixed before being fed into the reactor; the mixture is heated by the heat of hydrogen to the required temperature (300°C).

The reaction products consist of a higher alcohol, methanol,

small amounts of unconverted ester and by-products—hydrocarbons and water. This mixture leaves the top of reactor 7 together with the catalyst and excess hydrogen and separated in hot separator 8 into a liquid and a gas phase.

The gas phase gives up its heat to hydrogen in heat exchanger 3 and is additionally cooled by water in cooler 9; the condensate formed is separated from hydrogen in high-pressure separator 10. This hydrogen is returned to hydrogenation.

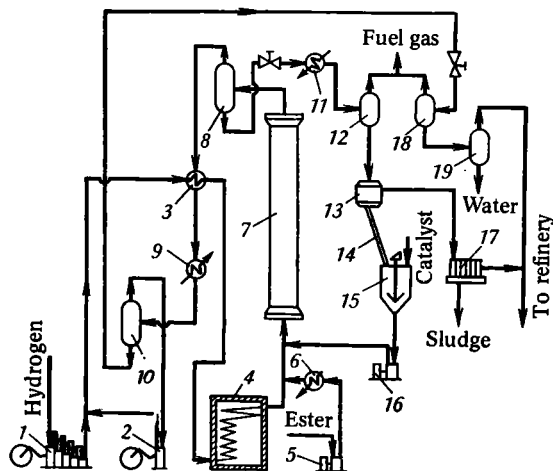


Fig. 7.17. Flow diagram of the hydrogenation of esters of higher acids to C₁₀-C₁₈ alcohols:

1, 2—compressors; 3—heat exchanger; 4—tubular furnace; 5, 16—pumps; 6—steam heater; 7—reactor; 8, 10, 12, 18, 19—separators; 9, 11—coolers; 13—centrifuge; 14—screw conveyor; 15—mixer; 17—press-filter.

The liquid phase from separator 8 is throttled to a pressure close to atmospheric, cooled by water in cooler 11 and separated in low-pressure separator 12 from the gas evolved upon throttling. The liquid passes to centrifuge 13, where larger catalyst particles settle out, entraining approximately a threefold amount of alcohols. This slurry is transferred by screw conveyor 14 to mixer 15, into which a fresh catalyst is introduced. The resultant mixture is fed into reactor 7 by means of pump 16. In this way, ≈ 85 percent of the catalyst is circulated and returned to the process. The remainder is in an extremely pulverized form (as a result of the attrition of the grains) and emerges from centrifuge 13 together with the major mass of the products and is filtered off from them on press-filter 17. This catalyst slurry is discharged.

The liquid phase from separator 10 is throttled and separated from the gas in low-pressure separator 18. The gas is combined with the

gas from separator 12 and used as a fuel gas. The liquid from separator 18 is separated from a small amount of water in separator 19, united with the product mixture after press-filter 17 and sent for further processing—the recovery of methanol, the saponification of the unconverted esters by alkali at 90 °C, the distillation of the higher alcohols in vacuum from the heavy residue (soap). The methanol is returned to the synthesis of the ester.

7.3.5. Technology of Gas-Phase Hydrogenation

The gas-phase hydrogenation process is carried out by passing a mixture of hydrogen with the vapours of the organic compound through a heterogeneous catalyst. This process is used for compounds, whose volatility at the reaction temperature is sufficient for bringing their partial pressure in the gas-vapour mixture to the required level. With a large excess of hydrogen, a high temperature or a reduced overall pressure the process can be employed to hydrogenate less volatile compounds. The process is widely used for the hydrogenation of benzene, phenol, nitrobenzene, aliphatic aldehydes and ketones, etc.

The vast majority of gas-phase hydrogenation reactions are carried out with a fixed catalyst in the form of beads, pellets or in other forms, the particle size being 3-5 mm. Only in rare cases is a finely dispersed catalyst used—for fluidized-bed processes.

Types of Reaction Apparatus. Because of the low coefficients for the transfer of heat from the gas to the wall, the heat-removal problem in gas-phase hydrogenation is much more complicated than in liquid-phase hydrogenation. It becomes even more complicated with a fixed bed of catalyst, whose grains hinder the diffusion of the reagents and their cooling. Depending on the degree of exothermicity of the reaction, the heat is removed by three principal methods; the choice of the method is dictated by the design features of hydrogenation reactors.

In tubular reactors used for carrying out strongly exothermic hydrogenation processes (the reduction of nitro compounds, the hydrogenation of aromatics), the catalyst is placed in tubes 25-50 mm in diameter (Fig. 7.18a). The vapour-gas mixture of hydrogen with the organic reagent is usually fed at the top (sometimes at the bottom) and the reaction takes place in the tubes on the catalyst grains. The heat evolved is removed by the cooling agent circulating in the intertubular space. The most suitable cooling agent is the boiling water condensate; in this case the reaction heat is used for the generation of steam.

In such units, the extent to which the reaction volume is used is not high, which is why less exothermic reactions are carried out

in vessels with a continuous catalyst bed placed on perforated trays or in special cases in several beds. Placed between the catalyst beds are coolers (just as is the case with the reactors shown in Fig. 7.15c but the vapour-gas mixture is supplied at the top). Sometimes, use is made of adiabatic reactors with a continuous catalyst bed and with intermediate cooling of the reaction mass. For even more weakly exothermic reactions (the hydrogenation of saturated aldehydes) only cold hydrogen is fed between the catalyst beds; the hydrogen takes up the extra heat (just as in the reactor shown in Fig. 7.15d). In the gas-phase hydrogenation of carboxylic acids or their esters to alcohols there is no need for cooling the reaction mixture.

For the operation at a high pressure use in some cases is made of reactors employed for the synthesis of ammonia. The catalyst is placed in several beds in a special catalyst case (Fig. 7.18b), which is assembled outside the reactor; it is withdrawn from the reactor and placed back when the catalyst is to be replaced. Cold hydrogen or the reaction mixture is introduced into the annular space between the reactor body and the catalyst case to remove part of the heat and to protect the reactor body from the action of high temperatures. Cold hydrogen is introduced at several points along the height of the catalyst case; all the pipes are connected through the massive lid and bottom rather than at the side of the reactor in order to prevent a decrease in the strength of the reactor body.

When the gas-vapour mixture is passed through the continuous catalyst bed, the temperature increases to a certain extent, which is why the height of the catalyst bed must be chosen so as to prevent excessive overheating and to keep the temperature within the permissible optimum limits. An important method of temperature control in gas-phase hydrogenation is to use a large excess of hydrogen as compared with the required theoretical amount. It ranges from 5 : 1 to (20-30) : 1, depending on the process. Excess hydrogen accumulates the heat evolved, preventing excessive overheating of the reaction mass. Naturally, for each particular case there is an

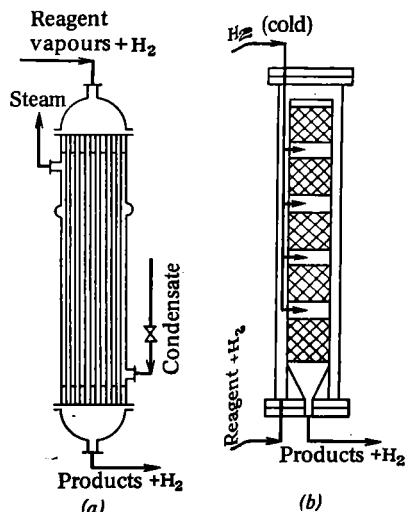


Fig. 7.18. Reaction units for vapour-phase hydrogenation:

a—tubular reactor; b—column with continuous beds of a heterogeneous catalyst and with cooling by cold hydrogen.

optimum excess of hydrogen, which is chosen with account taken of the cost of its recirculation.

It is interesting to combine the reactor for liquid-phase hydrogenation with a suspended catalyst with the reactor for gas-phase hydrogenation with a fixed catalyst, just as is the case shown in Fig. 7.16. Most of the reaction is accomplished in the first reactor, the heat being removed by one of the methods described above. The components of the mixture are vaporized in a hydrogen current and the hydrogenation is completed in the second reactor, which

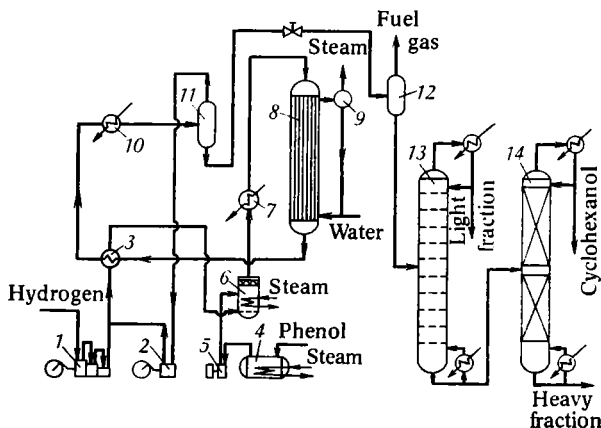


Fig. 7.19. Flow diagram of phenol hydrogenation:

1, 2—compressors; 3—heat exchanger; 4—tank; 5—pump; 6—vaporizer-saturator; 7—steam preheater; 8—reactor; 9—steam collector; 10—cooler; 11, 12—separators; 13, 14—fractionating columns.

does not require heat-exchange units. This scheme is especially suited for the hydrogenation of benzene to cyclohexane, when a nearly complete conversion of benzene is achieved at a high capacity of the reactor.

Flow Diagram of Gas-Phase Hydrogenation. All flow diagrams of gas-phase hydrogenation include a system of hydrogen compression and recirculation, its saturation with the vapours of the organic reagent, preheating of the mixture, the condensation and stepwise separation of the end product from hydrogen and volatile by-products (methane, etc.). The flow diagrams differ mainly in the step of separation of the liquid products and in the design of the reaction unit.

As a typical example, let us consider the flow diagram of the production of cyclohexanol by the hydrogenation of phenol. A simplified flow diagram of this process is given in Fig. 7.19. The hydrogenation is effected in a tubular reactor carrying a nickel catalyst on

a support (Al_2O_3 or Cr_2O_3) at 140-150 °C and 1-2 MPa. This reaction, the by-products of which are cyclohexane, cyclohexanone, cyclohexene and methane, has already been described (page 542).

Fresh hydrogen purified from mechanical impurities and catalyst poisons is compressed by compressor 1 to 1-2 MPa. The recycle hydrogen, which has lost some of its pressure in overcoming the hydraulic resistances in the pipes and vessels, is additionally compressed to the operating pressure by means of circulation compressor 2. Fresh hydrogen is mixed with recycle hydrogen and the mixture is heated in heat exchanger 3 by the reaction mixture emerging from the reactor and is led through a bubble-cap column to vaporizer-saturator 6. The phenol from tank 4 is also fed by means of high-pressure pump 5 into vaporizer-saturator 6. In order to avoid the crystallization of the phenol, tank 4 and the pipes for phenol are heated by steam.

The phenol level in vessel 6 and the temperature in it (120-125 °C) are controlled automatically in order to keep the composition of the gas-vapour mixture constant and to make it correspond to the optimum excess of hydrogen (a nearly tenfold excess with respect to the amount consumed on hydrogenation). The upper part of the vaporizer has a packing of Raschig porcelain rings, which serves as an entrainment trap. The vapour-gas mixture from the vaporizer-saturator passes through heater 7 and is led into the tubes of reactor 8. The heat evolved is removed by means of the boiling water condensate; steam having a pressure of 0.3 MPa can be used for process needs. The degree of conversion of phenol in the reactor is 85-99 percent.

The hot reaction gases from contact vessel 8 are run into heat exchanger 3, where they give up their heat to hydrogen. The gases are then additionally cooled by water in cooler 10, and the condensate formed is separated from hydrogen in high-pressure separator 11. The hydrogen is returned by means of circulation compressor 2 to hydrogenation. The condensate from separator 11 is throttled to atmospheric pressure and is separated from the gas (hydrogen + methane) in low-pressure separator 12, the gas being run into the fuel gas line.

The crude cyclohexanol containing unconverted phenol and also small amounts of cyclohexanone, cyclohexane, cyclohexene and water is led to columns 13 and 14 for fractionation. The last three compounds, which form an azeotrope, are distilled first during the vacuum fractionation. Then, cyclohexanol together with cyclohexanone is separated from the higher-boiling impurities and phenol; the latter being returned to hydrogenation. The presence of cyclohexanone as an impurity in the finished product is not troublesome, since upon further processing to caprolactam or adipic acid cyclohexanone gives the same products as cyclohexanol. The yield of

the end product is in excess of 96 percent with a selectivity of ≈ 98 percent.

The flow diagram of other gas-phase hydrogenation processes may be different in some respects. The vaporizer-saturator 6 and the reactor are sometimes built as a single unit; in operations involving more volatile compounds the vaporizer is not used at all. In the latter case, hydrogen and the liquid to be hydrogenated are simply mixed (in some definite proportions) before being led into heat exchanger 7. If the process is carried out in a reactor carrying several continuous catalyst beds, only part of hydrogen is heated, the remainder being run cold into the space between the catalyst beds. One of the products in the hydrogenation of some compounds is water. In order to separate it from the organic layer a separator is set up after vessel 12.

SYNTHESES BASED ON CARBON MONOXIDE

Organic synthesis based on carbon monoxide has been rapidly developed commercially for the last several decades. The reactions that are most frequently used in industrial practice are as follows:

(1) syntheses from carbon monoxide and hydrogen employed for the production of aliphatic hydrocarbons and alcohols;

(2) Oxo synthesis, hydroformylation and carboxylation, which have become important for the production of aldehydes, carboxylic acids and their conversion products (alcohols, esters, and other compounds).

The scale of production by syntheses based on carbon monoxide is very large, which is evidenced by the pattern of production in the USA (the forecast for 1980): $\approx 5,000,000$ tons of methanol; more than 1,000,000 tons of aldehydes produced by Oxo synthesis; 270,000 tons of butyl alcohols. The importance of these processes, especially of syntheses based on carbon monoxide and hydrogen, will undoubtedly increase to a considerable extent because of the shortage of petroleum and of the possibility of coal-based production.

8.1. Syntheses from Carbon Monoxide and Hydrogen

The catalytic conversions of CO and H₂ are varied, but two most important processes may be singled out: the synthesis of hydrocarbons, including fuel, and the production of alcohols, especially methanol.

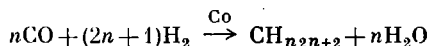
8.1.1. Synthesis of Hydrocarbons from CO and H₂

One of the well-known reactions of CO and H₂ is the formation of methane by catalysis over metallic nickel at 200-250 °C under pressure:

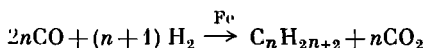


This *methanation process* is now intensively developed with a view to producing town gas from coal.

In the 1920s Fischer and Tropsch found that the catalytic condensation of CO and H₂ at a high pressure (10-15 MPa) with alkalis being added to metallic catalysts gives a mixture of oxygen-containing compounds, and when the pressure is reduced to 3 MPa the chief products obtained are hydrocarbons. With cobalt the reaction proceeds with the elimination of water:



and with iron the reaction involves the formation of carbon dioxide:



At that time carbon monoxide and hydrogen were made from coal, which is why the mixture of hydrocarbons produced was named *kogazin* and its gasoline fraction was given the name *synthine* (synthetic gasoline). Before 1945 in Germany this synthesis of motor fuel by the Fischer-Tropsch process was successfully used, but today there is only one or two plants in the world (South Africa) which produce a hydrocarbon fuel from coal. However, much effort is now devoted to the improvement of the process; it is very likely that the importance of this process will be revived in connection with the increasing shortage of crude oil.

The Fischer-Tropsch synthesis of hydrocarbons under moderate conditions is irreversible and is accompanied by the evolution of a large amount of heat (165-205 kJ or 39-49 kcal per CH₂ group in the hydrocarbon produced). The best catalyst was found to be iron (which is more heat-conducting and cheap) promoted with 0.5 percent of K₂O; the catalyst operates effectively at 220-320 °C and 1.5-2.5 MPa. There are two variants of the process—a fixed-bed process and a fluidized-bed process; the two processes employ an effective system of heat removal with cooling by a boiling water condensate and generation of high-pressure steam.

The products obtained consist of paraffinic and olefinic hydrocarbons, which are mostly of linear structure with the double bond at the end position; the products also contain a certain amount of oxygen-containing compounds (alcohols and ketones). By the fractional composition, the hydrocarbons are mixtures of lower homologues (C₃-C₄), gasoline, diesel fuel, soft and hard paraffin waxes. The group and fractional compositions of the products can be varied by changing the temperature, pressure and catalysts. For example, the synthesis can be directed to the predominant formation of isomeric hydrocarbons which have a higher octane number than linear α-olefins, etc. New catalysts have lately been patented, say molecular sieves (zeolites) for the selective synthesis of lower olefins (C₂-C₃) and even aromatic hydrocarbons from CO and H₂, which is an important factor for the future switch to a solid mineral fuel in organic synthesis.

8.1.2. Synthesis of Alcohols from CO and H₂. Methanol

It has been pointed out above that Fischer and Tropsch conducted the reaction between CO and H₂ at a high pressure and obtained a mixture of oxygen-containing compounds (*synthol*)—alcohols, aldehydes, ketones, carboxylic acids and esters. These compounds have not found application as synthetic fuels, but some new processes have been developed on the basis of the Fischer-Tropsch reaction. For instance, when iron promoted with oxides and alkalis is used at 160–190 °C and 20–30 MPa, the major products obtained are higher primary alcohols of linear structure, which contain, however, branched isomers and secondary alcohols. In the presence of zinc promoted with alkali at 400–475 °C and 20–40 MPa a mixture of lower alcohols is formed (beginning with methanol but with a preponderance of isobutyl alcohol). Of all these processes, only the synthesis of methanol has attained a major commercial significance.

Methanol is a colourless liquid (b.p. 64.7 °C) with an odour similar to the smell of ethyl alcohol. It is miscible with water and many organic liquids in all proportions. It is flammable, forms explosive mixtures with air (6–34.7 percent by volume) and is highly toxic.

Methanol was originally produced by the dry distillation of wood, but this method has been superseded by the synthesis from carbon monoxide and hydrogen employed currently on a large commercial scale in many advanced countries. Besides, methanol is one of the products in the gas-phase oxidation of lower paraffins.

The major proportion of methanol is consumed for the production of formaldehyde. It is also an intermediate in the synthesis of esters (methyl methacrylate, dimethyl terephthalate, dimethyl sulphate) and is used as a methylating agent (in the production of methylamines and dimethylaniline). A certain amount of methanol is employed as a solvent, but because of its high toxicity it is often replaced by other solvents. Besides, methanol is recommended as a component of motor fuel; it is also used for the production of a high-octane additive to fuel (methyl-*tert*-butyl ester) and is regarded as a promising intermediate for the synthesis of hydrocarbon fuels, lower olefins and other compounds (instead of their direct synthesis from CO and H₂).

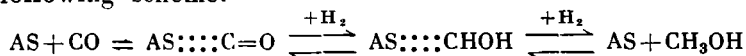
The formation of methanol from carbon monoxide and hydrogen is a reversible exothermic reaction:



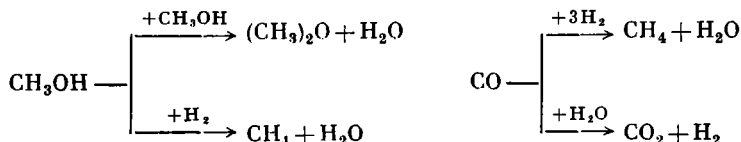
Because of the exothermicity of the process the equilibrium constant falls off with increasing temperature, being equal to 2.316×10^{-4} at 300 °C and to only 1.091×10^{-5} at 400 °C. It is for this

reason that the pressure has to be increased; an increase in pressure will favour the growth of the equilibrium degree of conversion due to a decrease in the volume of the gas mixture as a result of the reaction. The dependence of the equilibrium content of methanol in the reaction mixture on the total pressure at various temperatures is presented in Fig. 8.1. The synthesis of methanol from CO and H₂ was first developed by Patart in 1924, who used zinc oxide as the catalyst. Later, zinc oxide was activated with chromium oxide (8 mass parts of ZnO per 1 mass part of Cr₂O₃). Oxide copper-chromium and zinc-copper-chromium catalysts are more active, but a thorough purification of the reagents is required.

The mechanism of the formation of methanol is represented by the following scheme:



The by-products formed are dimethyl ether (as a result of the dehydration of methanol), methane (the hydrogenation product of methanol and CO), carbon dioxide and water:



There is also obtained a small amount of other alcohols, aldehydes and acetone, but the selectivity of the reaction to methanol in the presence of the catalysts indicated above is high, reaching 95 percent.

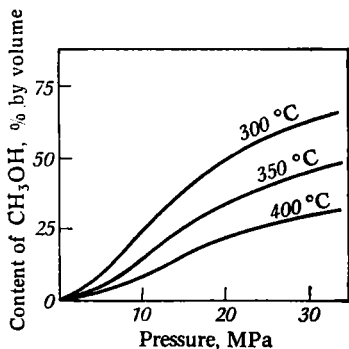


Fig. 8.1. Dependence of the equilibrium content of methanol in the reaction mixture on pressure and temperature (CO : H₂ = 1 : 2).

The choice of the process parameters is dictated by the requirements for high selectivity and intensity. The temperature depends mainly on the catalyst activity and may be varied within the range of 250-420 °C. The choice of the pressure depends on the temperature used; according to the thermodynamic characteristics, the pressure must be the higher, the higher is the temperature and it may vary from 5 to 20-35 MPa. It is obvious that a decrease in the pressure is favourable

since the power consumed for gas compression is reduced. Another factor favouring the reduction in power consumption is a

decrease in the recirculation of the unconverted gas, i.e., an increase in the actual degree of conversion of the reagents. However, the approach to the equilibrium degree of conversion is unfavourable because of the decrease of the capacity and selectivity. It is for this reason that the actual degree of conversion of the synthesis gas is limited to the value of 15-20 percent, which is attained at a contact time of 10-40 s.

The process was carried out for a long period of time at high pressures and temperatures (20-35 MPa and 370-420 °C) over an

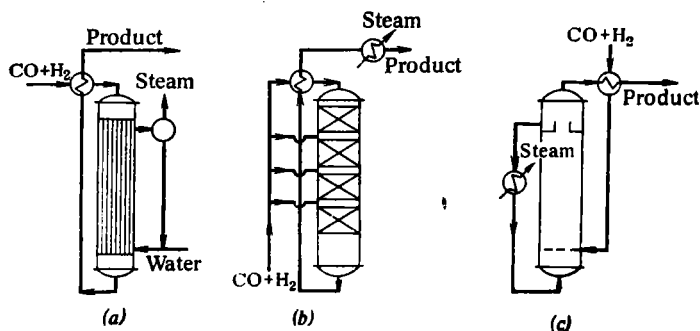


Fig. 8.2. Reaction units for the synthesis of methanol:

a—tubular reactor; *b*—adiabatic reactor with continuous catalyst beds and with the synthesis gas being fed into the space between them; *c*—reactor for liquid-phase synthesis (a “three-phase” system).

oxide zinc-chromium catalyst. More active catalysts based on $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ and $\text{ZnO} \cdot \text{CuO} \cdot \text{Cr}_2\text{O}_3$ with promoters added have only recently come into use owing to the thorough purification of the synthesis gas, which has made it possible to lower the temperature to 250-300 °C and the pressure to 5-10 MPa. This synthesis at a low pressure is replacing the older process operated at a high pressure; it has the advantage of the reduced power consumption for the gas compression.

Reaction Unit for Methanol Synthesis. The type of reaction unit depends on the method used to remove the heat and to carry out the reaction.

Wide use is made of tubular reactors (Fig. 8.2*a*) the tubes of which contain the catalyst, the reaction mass being cooled by the water condensate boiling in the intertubular space. The heat of the reaction gases is used to preheat the starting mixture. In this case, the highest exergy efficiency is attained and ≈ 1 ton of high-pressure steam is generated per 1 ton of methanol, but the amount of metal used for the reactor is large and the reaction space (the tubes) is only a small part of the total volume.

It is for this reason that adiabatic reactors carrying several (usually four) continuous catalyst beds (Fig. 8.2*b*) have become most im-

portant; no heat exchangers are used in these reactors and heat removal and temperature control are achieved by introducing the cold synthesis gas between the catalyst beds through special rhombic distribution grids which provide an effective mixing of the hot and cold gases. The temperature profile in such a reactor has a stepwise character; its gradual increase in the catalyst beds is replaced by a sharp drop when the hot gas is mixed with the cold gas. Only part of the starting synthesis gas is preheated; the remaining reaction heat is used for the generation of high-pressure steam. A somewhat modified scheme is more favourable from the standpoint of the exergy efficiency: only the required portion of the reaction gases is used to preheat the starting gas, the major proportion of the gases being sent to the waste-heat boiler.

Another method has recently been developed; it is known as the *synthesis in a three-phase system* (Fig. 8c). The process is effected in the liquid phase of an inert hydrocarbon in the presence of a heterogeneous catalyst suspended in the liquid, the synthesis gas being bubbled through this catalyst suspension. The heat of the reaction is removed by way of recirculation of the liquid through a steam generator or with the aid of internal heat exchangers containing the boiling water condensate. Methanol (and part of the hydrocarbon) are carried away by the unconverted synthesis gas; their heat is used to preheat the gas feed. The advantage of this method is that it provides an equilibrium state, more favourable for the synthesis in the liquid-phase reaction, which makes it possible to attain a 15-percent (by volume) concentration of methanol instead of the 5-percent concentration in the ordinary synthesis and the degree of conversion of the synthesis gas is 35 instead of 15 percent. This reduces the recycle of the gas and the power consumption.

The present-day plants used for the production of methanol have a high capacity and employ more perfect power-technological schemes. They are usually combined with the production of the synthesis gas at a pressure of 2-3 MPa, in which case it is more economical to purify the synthesis gas from the impurities by absorption with methanol at the pressure indicated. The synthesis gas is often purified from CO_2 , but in some plants CO_2 is left in the gas and allowed to participate in the formation of methanol. The optimum molar ratio of $(\text{H}_2 + \text{CO}_2) : (\text{CO} + \text{CO}_2)$ is $(2.05-3) : 1$. The high-pressure steam generated during the heat utilization is used to drive the turbocompressors, and the exhaust steam from the turbines is consumed for the conversion of the hydrocarbons to the synthesis gas and for the fractionation of the products.

Flow Diagram of Methanol Synthesis. The flow diagram of the process is shown in Fig. 8.3. The purified synthesis gas is compressed by turbocompressor 1 to 5-10 MPa and mixed with the recycle gas, which is compressed to the operating pressure by means of circulation

turbocompressor 2. The mixture is passed through adsorber 3, where the gas is purified from iron pentacarbonyl. This compound results from the interaction of CO with the iron of the apparatus and decomposes in the reactor with the formation of finely dispersed iron, which catalyzes the undesirable reactions in the production of CH_4 and CO_2 . For this reason and also because of hydrogen corrosion, the reactor is constructed of alloy steel.

The gas leaving the adsorber is split into two streams: one is heated in heat exchanger 4 and led to the upper part of reactor 5 for

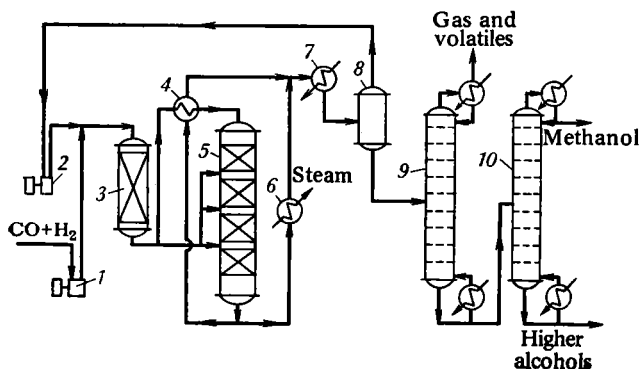


Fig. 8.3. Flow diagram of methanol synthesis:

1—turbocompressor; 2—circulation turbocompressor; 3—adsorber; 4—heat exchanger; 5—reactor; 6—steam generator; 7—cooler; 8—high-pressure separator; 9, 10—fractionating columns.

the synthesis and the other is run cold to reactor 5, where it flows between the catalyst beds to provide temperature control and heat removal. The gas moves downwards through all the catalyst beds and leaves the reactor at $\approx 300^\circ\text{C}$.

This gas is also divided into two streams: one passes through heat exchanger 4 and is used to preheat part of the starting mixture to the synthesis temperature and the other is sent to steam generator 6, where its heat is used for the generation of high-pressure steam. The gas streams are then united and cooled in cooler 7, where methanol is condensed and separated from the gas in high-pressure separator 8. The gas from the top of the separator is additionally compressed by circulation compressor 2 and returned to the synthesis stage.

The condensate from the bottom of the separator is throttled to a pressure close to atmospheric, and in fractionating column 9 the methanol is isolated from the dissolved gases and volatile products (dimethyl ether), which are then burned. In the next fractionating column 10 the methanol is distilled off from a small portion of heavy

impurities (higher alcohols), which are also burned. The resultant commercial methanol has a high degree of purity (up to 99.95 percent) and is produced in a yield of up to 95 percent with account taken of all the losses.

8.2. Oxo Synthesis

This reaction was discovered by Otto Roelen in 1938 and the first plant was started in 1948. Today the capacity of Oxo synthesis plants in the world exceeds 4,000,000 tons. The process serves as the basis for the production of aldehydes and the products of their conversion, mainly primary alcohols.

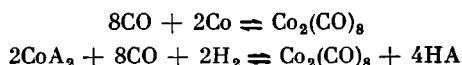
8.2.1. Chemistry and Scientific Foundations of the Process

The Oxo process consists of the interaction of olefins with $\text{CO} + \text{H}_2$ and of the formation of aldehydes:

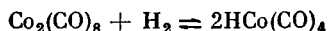


This involves the addition of the formyl group $-\text{CHO}$ and hydrogen at the double bond; the reaction is therefore also called *hydroformylation*. It is irreversible and is accompanied by the evolution of a large amount of heat; the amount of heat evolved varies from 117 to 147 kJ/mol (28-35 kcal/mol), depending on the olefin used.

Originally the Oxo synthesis made use of metallic cobalt as the catalyst, but it was soon found that the best catalysts are cobalt carbonyls. The catalysts most widely used are dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$, which is formed from metallic cobalt or its salts by the action of CO or CO and H_2 under pressure:



and cobalt hydrocarbonyl obtained from cobalt octacarbonyl and hydrogen:



The reactions leading to these carbonyls are reversible, and when the pressure is reduced the carbonyls are decomposed, which is why it is necessary to employ a high pressure, which is 10-30 MPa when the cobalt carbonyls are used for the reaction as the catalysts. In order to lower the pressure and to improve the other process parameters, modified cobalt catalysts containing a trialkylphosphine ligand have been lately proposed:



This catalyst complex is relatively stable to decomposition, which allows the synthesis pressure to be reduced to 5-10 MPa, but it is less active and causes the hydrogenation of the olefin and aldehyde. With this catalyst the process can be directed to the formation of an alcohol.

Much attention has been attracted to the most stable and active hydrocarbonyl complexes of rhodium. Of these, $\text{HRh}(\text{CO})_4$ has a very

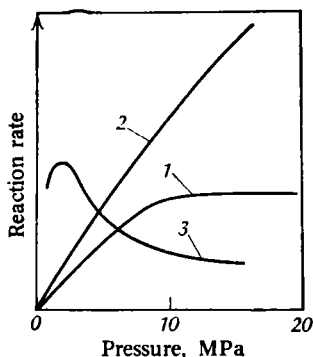


Fig. 8.4. Dependence of the rate of hydroformylation of olefins on pressure at a $\text{CO} : \text{H}_2$ ratio of 1 : 1:

1—dependence on the total pressure; 2—dependence on the hydrogen pressure at constant partial pressure of carbon monoxide (5 MPa); 3—dependence on the pressure of carbon monoxide at constant partial pressure of hydrogen (5 MPa).

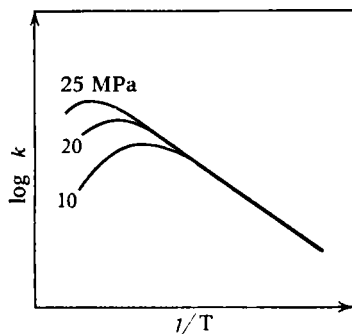


Fig. 8.5. Dependence of the rate of hydroformylation of olefins on temperature at different pressures.

high isomerizing ability, and the most interesting complex is one-modified by the phosphine ligands, $\text{HRhCO}(\text{PR}_3)_3$, where R is the phenyl, alkyl or ArO and RO groups. The reaction in the presence of these complexes proceeds at 0.1-5 MPa.

The mechanism and kinetics of the hydroformylation reaction have been studied most thoroughly with cobalt carbonyls used as the catalysts. There is observed a complicated dependence of the reaction velocity on the partial pressure of the reagents and temperature. With a $\text{CO} : \text{H}_2$ ratio of 1 : 1, other conditions being equal, the reaction rate at low pressures is low and increases linearly when the total pressure increases up to 10 MPa, and then remains constant (Fig. 8.4, curve 1). If the partial pressure of carbon monoxide is maintained constant, the rate of hydroformylation is found to be proportional to the hydrogen pressure (curve 2). With the hydrogen pressure being kept constant the dependence of the reaction velocity on the partial pressure of carbon monoxide becomes complicated.

(curve 3). With a low partial pressure of carbon monoxide, P_{CO} , an increase in this pressure increases the reaction velocity but when a certain limit is reached there appears a maximum, following which the reaction rate decreases with increasing P_{CO} . This opposite effect of the reagents evidently accounts for the fact that the rate of the process is independent of the total pressure when it exceeds a certain value characteristic of each operating temperature.

The effect of the temperature on the rate of hydroformylation is also unusual (Fig. 8.5). With other conditions being constant and at sufficiently low temperatures this dependence is described by the Arrhenius equation, from which the activation energy is calculated; it varies from 63 to 83 kJ/mol (15-20 kcal/mol), depending on the olefin used. As the temperature increases further the reaction rate increases but slowly and then decreases after it passes through the maximum. The maximum is reached with the temperature being the lower, the lower is the pressure.

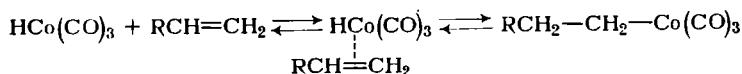
As regards the effect of the amount of the catalyst and of the olefin concentration (the partial pressure), the reaction rate has been found to depend linearly on these parameters. Thus, the hydroformylation reaction is first-order in the olefin, hydrogen and the catalyst and depends in a complicated manner on the pressure of carbon monoxide:

$$r = k \frac{C_{\text{cat}} P_{\text{olef}} P_{\text{H}_2}}{1 + K P_{\text{CO}}}$$

These relationships are well accounted for by the following mechanism, which is typical of metal-complex catalysis. When cobalt is used in the form of its salt, the formation of the carbonyl and hydrocarbonyl occurs by the reactions given above, which accounts for the self-acceleration of the process, the effect of the partial hydrogen pressure and the increase of the rate at a low partial pressure of CO. An active complex is the hydrocarbonyl, which is capable of dissociation with the liberation of CO and formation of a coordinately unsaturated cobalt hydrotricarbonyl:

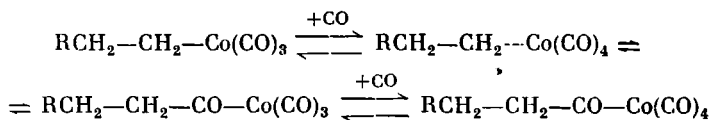


This accounts for the retarding effect of CO at its increased partial pressure. This complex is then coordinated with the olefin molecule and is converted to cobalt alkylcarbonyl by the mechanism of insertion at the Co—H bond:



The resultant complex, which is coordinately unsaturated, unites with CO and there again occurs the intracomplex insertion reaction

at the Co—C bond leading to cobalt acylcarbonyl:

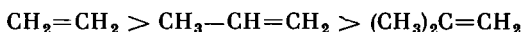


Cobalt acyl-, tri- and tetracarbonyls form aldehydes under the influence of hydrogen or cobalt hydrocarbonyl; for example,

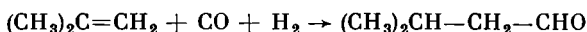


The heptacarbonyl formed is converted to cobalt hydrocarbonyl by the action of CO and H₂.

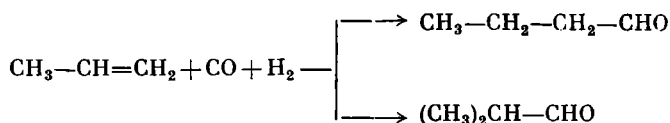
The reactivity of olefins in the Oxo synthesis varies in the following order:



The resultant formyl group preferentially adds on to the least substituted carbon atom at the double bond, which is characteristic of many reactions of metal-complex catalysis. As a result, isobutylene gives only one aldehyde:

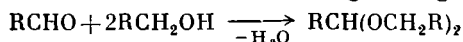


but propylene and other olefins with a linear carbon-atom chain give two isomeric aldehydes:

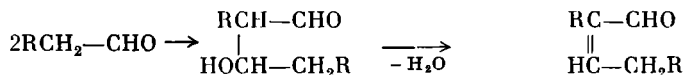


The ratio of normal aldehydes to isaldehydes is very important since it is *n*-aldehydes and the primary alcohols of linear structure obtained from them that are of practical value. This ratio increases with decreasing temperature and total pressure and also with increasing partial pressure of hydrogen, but in this case either the rate of the process falls off or the side hydrogenation reaction becomes noticeable. The effect of the nature of the catalyst has been found to be the strongest. With cobalt carbonyls the ratio of normal to isaldehydes is (3-4) : 1; with cobalt hydrocarbonyl modified by trialkylphosphine the ratio increases up to (7-8) : 1, and with modified rhodium hydrocarbonyl it increases even to (12-15) : 1. The increase of the yield of normal aldehydes is an important advantage of the modified catalysts over the traditional cobalt carbonyls.

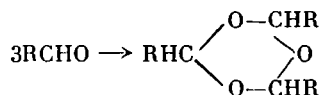
Apart from the hydrogenation of aldehydes and olefins, the Oxo synthesis involves other side reactions. The alcohols formed may undergo condensation with aldehydes and give high-boiling acetals:



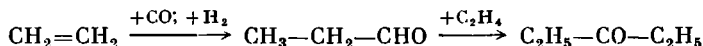
Other by-products (aldols) result from the aldol condensation of aldehydes, in which case the elimination of a water molecule from the aldol results in the formation of an unsaturated aldehyde:



Some of the by-products are cyclic polymers of aldehydes:



The hydroformylation of ethylene gives by-product diethyl ketone, which is presumably formed as a result of the further interaction of the aldehyde with ethylene:

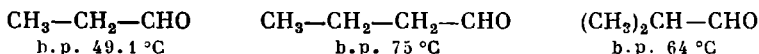


The yield of by-products increases in all cases with increasing temperature, and this circumstance plays an important role in the choice of the optimum temperature for the process.

8.2.2. Technology and Products of Oxo Synthesis

The end products of Oxo synthesis are aldehydes or the corresponding alcohols, which are formed as a result of the hydrogenation of aldehydes. Hydroformylation and hydrogenation are therefore combined into a single technological process, which gives (if required) both aldehydes and alcohols.

Aldehydes and Alcohols Produced by Oxo Synthesis. Of the aldehydes produced by Oxo synthesis, the following are of practical value: *propionaldehyde*, *n-butyraldehyde* and *isobutyraldehyde*, which are obtained by the hydroformylation of ethylene and propylene:

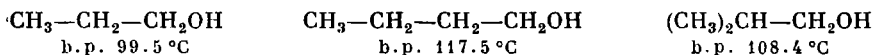


These compounds are all liquids sparingly soluble in water. These aldehydes were once obtained by the oxidation or oxidative dehydrogenation of the corresponding alcohols, which were not readily available. Oxo synthesis has become the most economical route to their production.

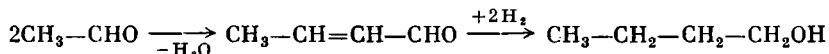
The aldehydes indicated above are used as intermediates for organic synthesis. They are oxidized to give propionic, butyric and isobutyric acids, of which propionic acid is especially important: it is used for the synthesis of valuable pesticides. The outlet for *n*-butyraldehyde is in the manufacture of a polymeric material—polyvinyl butyral. Propionaldehyde and *n*-butyraldehyde are the

feedstocks for the production of polyhydric alcohols that are substitutes for glycerol—trimethylolethane, $\text{CH}_3\text{—C}(\text{CH}_2\text{OH})_3$, and trimethylolpropane, $\text{CH}_3\text{—CH}_2\text{—C}(\text{CH}_2\text{OH})_3$. *n*-Butyraldehyde is used to obtain 2-ethylhexyl alcohol, whose phthalate is an effective plasticizer for polymers.

Oxo synthesis is very important for the manufacture of the hydrogenation products of the aldehydes mentioned above—*n*-propyl, *n*-butyl and isobutyl alcohols:



Formerly, *n*-propyl alcohol was not readily available, isobutyl alcohol was obtained from the synthesis gas (CO and H_2) under pressure (page 563), and *n*-butyl alcohol was prepared by a multistep synthesis from acetaldehyde; this method is still of some value at present:



Oxo synthesis is the most economical method of production of these alcohols because the process involves only a few steps, the raw material is available and the yield of the alcohols is high.

The alcohols mentioned are used as solvents; they are also used as solvents in the form of their esters with acetic acids (especially *n*-butyl acetate). Besides, *n*-butyl alcohol is used as the feedstock for the production of tributyl phthalate (a plasticizer) and tributyl phosphate (an extractant).

The alcohols in the $\text{C}_7\text{—C}_9$ range, which are intermediates for the production of ester plasticizers, especially phthalates, are produced by Oxo synthesis from olefins ($\text{C}_6\text{—C}_8$) obtainable by thermal cracking of paraffin wax or by organoaluminium synthesis, from propylene and isobutylene dimers and from the codimer of propylene and butylenes. The plasticizing ability of the esters of these alcohols are similar to that of the esters of 2-ethylhexanol, and the method of their synthesis is more economical than the synthesis of 2-ethylhexanol. Another route to $\text{C}_7\text{—C}_9$ alcohols, which consists of the hydrogenation of fatty acids obtainable by the oxidation of paraffins is also less economical than Oxo synthesis. For these reasons, the production of $\text{C}_7\text{—C}_9$ alcohols from olefins, CO and H_2 becomes increasingly important as an industrial process.

Primary alcohols of linear structure in the $\text{C}_{10}\text{—C}_{18}$ range which serve as raw materials for the manufacture of detergents of the alkyl sulphate type, are produced on an ever increasing scale by Oxo synthesis from α -olefins obtainable by thermal cracking of paraffin wax and by organoaluminium synthesis. Because of the biodegradability problem in the detergent industry these alcohols must have a linear carbon chain, which is successfully achieved by catalyzing the

hydroformylation reaction by a modified cobalt catalyst. A small amount of impurity isoalcohol (with the methyl group in position 2) does not practically affect the biodegradability and is more than compensated by the high efficiency of Oxo synthesis as compared with the other methods of manufacture of higher primary alcohols (the hydrogenation of fatty acids provided by the oxidation of paraffin wax and by organoaluminium synthesis). For this reason, the production of alcohols in the C_{10} - C_{18} range, which are used as the feedstock for the manufacture of detergents by Oxo synthesis, has been developed in many industrially advanced countries.

Reaction Unit and Catalyst Regeneration. The hydroformylation reaction is carried out in a heterogeneous medium by bubbling the mixture of CO and H_2 through the liquid reaction mass. These gases are sparingly soluble in organic liquids, and for the diffusion resistances to be overcome it is very important that the mixture be stirred sufficiently strongly. It is attained by using an excess of the CO : H_2 mixture; the recycle coefficient (the ratio of the recycle to the fresh synthesis gas) is (2-3) : 1. The mixture of CO and H_2 is taken in a stoichiometric ratio (1 : 1) required for Oxo synthesis.

It has already been pointed out that the selectivity of the reaction increases with decreasing temperature. Besides, it must be kept in mind that most of the side reactions follow the formation of aldehydes. In order to reduce their role, it is important that conditions be provided under which the rate of hydroformylation would be high and the rate of the condensation of aldehydes low. This is attainable due to the incomplete conversion of olefins and by using solvents—the by-products of the reaction (the still bottoms from distillation, which contain trimers of aldehydes, alcohols, etc.) and also various hydrocarbons (say, toluene and pentane-hexane fractions).

The choice of the remaining parameters, namely the pressure, temperature and catalyst concentration, depends on the type of the catalyst used:

Catalyst	$HCo(CO)_4$	$HCo(CO)_3PR_3$	$HRhCO(PR_3)_3$
Pressure, MPa	20-30	5-10	0.7-2.5
Temperature, °C	110-160	150-200	60-100
{ Concentration of metal, weight percent on olefin	0.1-1	0.5-1	0.01-0.1

Despite the low concentration of the catalysts, the high cost of the metals calls for their regeneration, which is closely associated with the design of the reaction unit.

The process was originally carried out using metallic cobalt deposited on kieselguhr suspended in the liquid phase. With CO, H_2 and the olefin being fed the cobalt is converted to soluble cobalt carbonyls and hydrocarbonyl, which catalyze the reaction. The reaction mass

together with kieselguhr, which has lost a greater part of cobalt, overflows into another vessel, where at reduced pressure with hydrogen being introduced the cobalt carbonyls decompose to the metal, which is again adsorbed on kieselguhr and recycled to the hydroformylation reactor.

Later, this method of regeneration of the catalyst (by decomposing it to the metal and depositing on a support) was realized in the

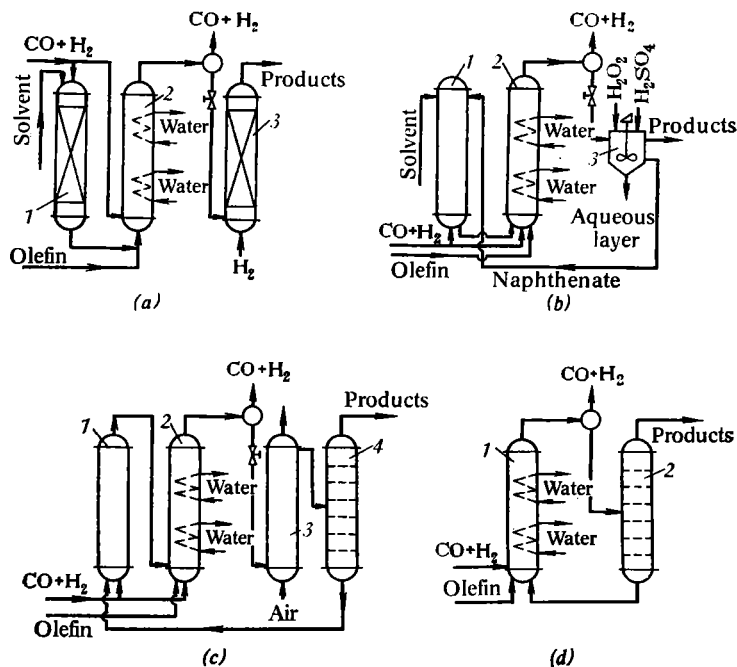


Fig. 8.6. Reaction units and flow diagrams for the regeneration of the catalysts in hydroformylation processes:

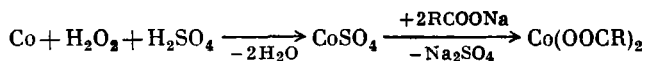
a—triad flowsheet (1—catalyzer; 2—reactor; 3—decatalyzer); b—extraction-salt flowsheet (1—carbonyl-formation unit; 2—reactor; 3—oxidation-extraction unit); c—evaporation-salt flowsheet (1—carbonyl-formation unit; 2—reactor; 3—oxidation column; 4—vaporizer); d—evaporation flowsheet (1—reactor; 2—vaporizer).

so-called *triad scheme*, which is still used at present (Fig. 8.6a). The reaction unit consists of three columns designed for operation at a high pressure. Two columns are filled with a fixed pumice packing and the third functions as the reactor and is a hollow bubble-cap column fitted with cooling facilities, with the aid of which steam is generated by using the heat of the reaction. The packed columns called the catalyzer and decatalyzer (or the cobaltizer and decobaltizer) alternate their functions, which consist, respectively, of the

formation of a homogeneous solution of cobalt carbonyls and the adsorption of cobalt after the decomposition of the carbonyls. The solvent and a small portion of the CO : H₂ mixture are fed into the catalyzer carrying pumice enriched with cobalt. Metallic cobalt is converted into soluble carbonyls, the solution of which is passed to the reactor, into which are introduced the olefin and the major proportion of the CO : H₂ mixture, and the hydroformylation is carried out.

The reaction mass overflows into the decatalyzer, where at reduced pressure and with hydrogen being fed the carbonyls are decomposed and cobalt is deposited on pumice. When the amount of cobalt is exhausted in the catalyzer and after it is accumulated in the decatalyzer the stream consisting of the olefin, the solvent and a small amount of the CO : H₂ mixture is reversed—the decatalyzer begins to function as the catalyzer and vice versa. The disadvantages of the triad system are as follows: the high capital cost for the reaction unit, where the reaction occurs only in one of the columns and the reversal of the streams, which complicates the automation of the process.

The so-called *salt* (or *naphthenate*) *processes* have become most popular in recent years; cobalt is regenerated in the form of salts rather than of the metal. In order to convert the null-valent cobalt to a salt use must be made of oxidizing agents, which may be hydrogen peroxide and even air. In one process (Fig. 8.6b), the liquid reaction mass is extracted by an aqueous solution of hydrogen peroxide and sulphuric acid and the cobalt passes over into the aqueous layer in the form of the sulphate. The aqueous layer is treated with the salt of naphthenic acid and cobalt naphthenate is obtained:



The cobalt naphthenate is separated from the aqueous solution and led to the carbonyl-formation unit, where it is converted to the carbonyls under the action of the CO : H₂ mixture. It has been found that sulphuric and naphthenic acids may be replaced by acetic acid, in which case the carbonyls can be obtained from a mixture of an aqueous solution of cobalt acetate and a hydrocarbon solvent.

In another salt process (Fig. 8.6c) the liquid reaction mass is oxidized by air at 40-70 °C and 0.2-0.4 MPa without addition of water and acids. In this process, a small portion of the aldehyde gives a peracid, which oxidizes the cobalt to the salt of the corresponding acid. The salt is isolated in the form of a solution in the by-products or in a foreign solvent, sufficiently volatile aldehydes being distilled off and transferred to the carbonyl-formation unit and then to the hydroformylation reactor. This method of separation of the products and the catalyst is most attractive.

It is especially applicable for modified cobalt and rhodium catalysts which are sufficiently stable to decomposition. In such cases (Fig. 8.6d) neither carbonyl-formation unit nor oxidizing column is required, and the liquid reaction mass is directly led to the vaporizer. In the vaporizer, the volatile products are distilled off at reduced pressure and the catalyst solution from the bottom of the column is returned to the hydroformylation stage. The amount of the catalyst lost is at a minimum, which is especially important when the very expensive rhodium catalyst is used.

Flow Diagram of Oxo Synthesis. The Oxo synthesis technology have employed all the above-described methods of carrying out the

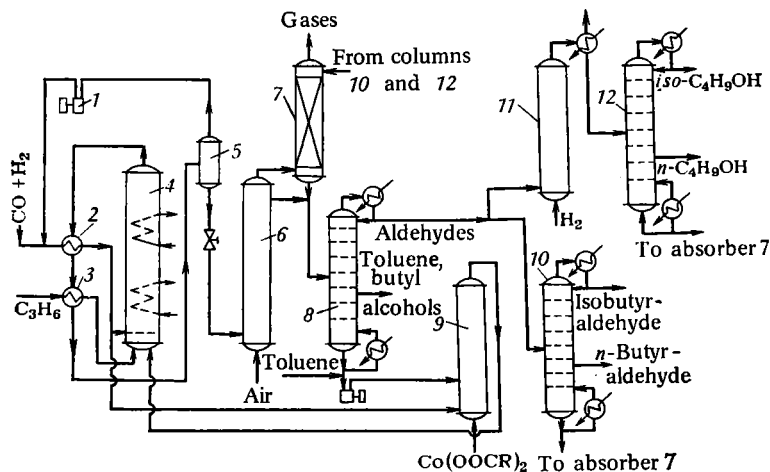


Fig. 8.7. Flow diagram of Oxo synthesis of butyraldehydes and butyl alcohols: 1—circulation compressor; 2, 3—heat exchangers; 4—reactor; 5—separator; 6—oxidation column; 7—absorber; 8—vaporizer; 9—carbonyl-formation unit; 10, 12—fractionating columns; 11—hydrogenation reactor.

reaction and of catalyst regeneration and also the processes involving cobalt and modified cobalt and rhodium catalysts. However, rhodium is very expensive and the modified cobalt catalyst is less active and causes a side hydrogenation reaction. Therefore, the overwhelming majority of Oxo plants operate in the presence of the conventional cobalt catalyst. The most promising method with this catalyst is the vaporization-salt method for carrying out the reaction and for the regeneration of the catalyst.

One of the present-day flow diagrams of the Oxo synthesis of butyraldehydes and butyl alcohols is shown in Fig. 8.7. The liquid propylene fraction and also the fresh synthesis gas at a pressure of 25-30 MPa and the recycle synthesis gas compressed to the same pressure by circulation compressor 1 are preheated, respectively,

in heat exchangers 2 and 3 by the heat of the hot reaction mass. They are then led to reactor 4, into which the solution of cobalt carbonyls in toluene and the heavy residues from the distillation products are led from carbonyl-formation unit 9. In reactor 4 aldehydes and by-products are formed at 110-160 °C, the heat evolved being dissipated by water or by the boiling water condensate (depending on the temperature) with the generation of low-pressure steam.

The heat of the reaction mass is used in heat exchangers 2 and 3, and in separator 5 the liquid is separated from the synthesis gas, which is recycled together with some of the unconverted propylene by compressor 1 to the reaction. The liquid from the separator is throttled to 0.2-0.4 MPa and is oxidized at 40-70 °C by a small amount of air in oxidation column 6 (the decobaltizer). In this column, the oxygen-depleted air passes over into the gas phase together with CO, H₂ and propylene, which were in dissolved state at a high pressure, and also with the vapours of the aldehydes entrained by the gas. These vapours are absorbed in absorber 7 by the heavy bottoms from distillation and the gases are discharged to the atmosphere or burnt.

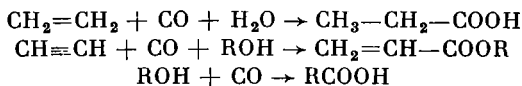
The liquid from oxidizing column 6 and absorber 7 is then run to vaporizer 8, where the solution of the cobalt salt in the heavy by-products are subjected to distillation and the crude aldehydes are taken overhead; the by-product butyl alcohols together with toluene are taken as the middle fraction. The solution of the cobalt salt from the bottom of this column with the recycle toluene added to it is sent to carbonyl-formation unit 9, where in the presence of a small amount of the CO : H₂ mixture and a fresh solution of cobalt naphthenate (to make up for the loss of the catalyst) the formation of the carbonyls takes place at 170-180 °C and 25-30 MPa. The resultant carbonyls are then led to reactor 4. The mixture of butyl alcohols with close-boiling toluene, which is taken from the middle part of column 8, is separated additionally (not shown in the flow diagram) into butyl alcohols and toluene, the latter being returned for the preparation of the carbonyls.

The crude aldehydes from the top of column 8 may be processed to pure aldehydes or alcohols. In the first case, they are subjected to fractionation in column 10 to produce commercial isobutyraldehyde and *n*-butyraldehyde. The remaining quantity (or all the crude aldehydes) are hydrogenated over a heterogeneous catalyst in reactor 11 and the resultant isobutyl and *n*-butyl alcohols are separated from the bottoms in fractionating column 12.

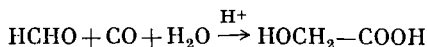
The vaporization-salt scheme is not suitable for the synthesis of alcohols in the C₇-C₉ and C₁₁-C₁₈ ranges because of the low volatility of the products. In these cases, use is therefore made of the triad or water-extraction schemes for the regeneration of the catalyst.

8.3. Synthesis of Carboxylic Acids and Their Derivatives Based on Carbon Monoxide

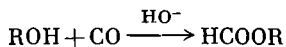
Using nickel carbonyl (or nickel halides, which form the carbonyl during the course of the reaction), Reppe extended Oxo reactions to acetylene, alcohols and ethers and found that the role of hydrogen (proton) donors can be played not only by molecular hydrogen but also by water, alcohols, mercaptans, amines, etc. In such cases, the products are carboxylic acids or their derivatives (*carboxylation* or *carbonylation*) rather than aldehydes:



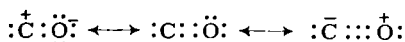
These reactions (except the syntheses from acetylene) are also catalyzed by strong mineral acids which are capable of involving aldehydes into analogous processes apart from the compounds mentioned above:



Finally, there are reactions of carbon monoxide which are accelerated by bases and which also belong to the category of carboxylation processes:



Such a varied reactivity of carbon monoxide is ascribed to its molecular structure, which is best described by three resonating structures:



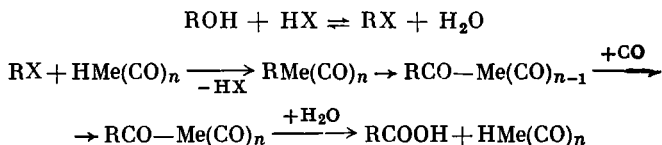
It should therefore be expected that carbon monoxide is capable of interacting also with electrophilic reagents, with which it reacts as an electron donor, and with bases, which supply it with missing electrons. This also accounts for the complex-forming ability of carbon monoxide and for the catalysis of its conversions by metal carbonyls.

8.3.1. Processes Catalyzed by Transition-Metal Complexes

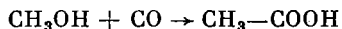
The reactions of carbon monoxide catalyzed by transition-metal carbonyls in the presence of various promoters are similar to the Oxo processes considered above. Of these reactions, the production

of acrylic acid or its esters has lost its practical value because of the use of expensive acetylene and of the availability of the more economical method of propylene oxidation. But the process is still used at present for the production of acids from alcohols and olefins.

The *carbonylation of alcohols* catalyzed by metal complexes has an advantage over acid catalysis since in the latter case there are formed many by-products of alcohol dehydration (olefins and ethers) and also of isomeric acids. Reppe was the first to accomplish these reactions with the aid of nickel carbonyls and promoters, the role of which was played by iodine and its salts, halogen derivatives, etc. Cobalt, iron, palladium and especially rhodium carbonyls are also active but only in the presence of the same promoters. The role of these promoters is accounted for by the intermediate formation of alkyl halides, which then undergo carbonylation by a mechanism close to that of Oxo synthesis:



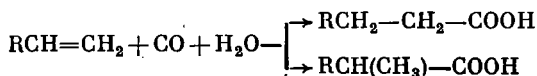
The process is strongly exothermic and is noted for a strong corrosion of the apparatus material. It has been commercialized for the production of acetic acid from methanol:



The use of cobalt salts and iodine (as the promoter) requires a temperature of 250 °C and a pressure of 70-75 MPa; the yield of acetic acid is ≈ 90 percent based on methanol.

Later, a process was developed in the USA, which was based on rhodium and iodine compounds; the pressure is as low as 0.1-0.5 MPa and the yield of acetic acid reaches 99 percent based on methanol. This method allows the production of acetic acid to be based on methane or on more available hydrocarbons (hydrocarbon $\rightarrow$ synthesis gas $\rightarrow$ methanol $\rightarrow$ acetic acid) and on coal (coal $\rightarrow$ water gas $\rightarrow$ methanol $\rightarrow$ acetic acid). According to some estimates, it is the most economical of the methods used for the production of acetic acid.

The *hydrocarboxylation of olefins* in the presence of transition-metal complexes is of interest because, in contrast to acid catalysis, acids of linear structure with an impurity of methyl-branched acids are predominantly formed from α -olefins (cf. Oxo synthesis of aldehydes):

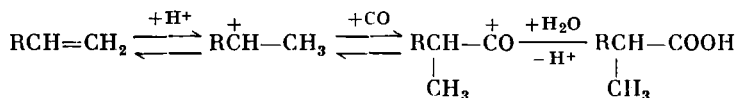


Analogously, when alcohols are used instead of water, esters of the same acids are formed (*hydrocarboalkoxylation*).

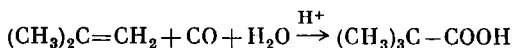
The reactions are catalyzed by metal carbonyls, especially cobalt carbonyls, in the presence of promoters such as pyridine and iodine. Catalytic systems based on palladium are also active. The information on the industrial application of this process has not been disclosed.

8.3.2. Acid-Catalyzed Processes

The acid catalysis of reactions involving carbon monoxide has assumed industrial importance mainly for the synthesis of carboxylic acids from olefins. The mechanism of the reaction consists of the preliminary protonation of an olefin by an acid with the formation of a carbonium ion, the interaction of the carbonium ion with CO leading to the acylium cation, and of the reaction of the acylium cation with water with the formation of a carboxylic acid:



The addition of hydrogen and the carboxyl group across the double bond on acid catalysis proceeds according to the Markovnikov rule. As a result, only ethylene gives unbranched propionic acid, and its homologues give α -methyl-branched acids. This method is of special interest for the synthesis of tertiary acids (neoacids) from iso-olefins, carbon monoxide and water. For example, from isobutylene there can be obtained *trimethylacetic acid*:



and the dimer or trimer of propylene give neoacids in the C_7 - C_{10} range. Neoacids and their salts display an unusually high solubility and viscosity as compared with other fatty acids, and their esters are highly stable towards hydrolysis, which is why they have found wide application in a number of fields.

The synthesis of carboxylic acids from olefins and CO can be carried out in the gas phase in the presence of supported phosphoric acid as the catalyst under severe conditions: $\approx 300^\circ\text{C}$ and 20-30 MPa. The side reactions involved are the formation of esters and the polymerization of the olefin, which is why there is required a large excess of CO with respect to the olefin.

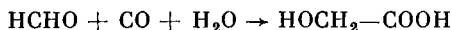
The synthesis of neoacids in the liquid phase under relatively mild conditions was originally accomplished in the presence of concentrated sulphuric acid (the Koch reaction) and found industrial application in a number of countries. The process involves two steps. In

the first step, the olefin and CO are passed through 95-100-percent sulphuric acid at 0-50 °C and 2-10 MPa and acylsulphuric acid, RCOOSO_2OH , is formed. The basic condition for the successful realization of this step is the use of an excess of the acid and carbon monoxide with respect to the olefin. The second step involves the treatment of the resulting solution with water, which leads to the hydrolysis of acylsulphuric acid and to the formation of a neoacid. The neoacid is separated from sulphuric acid by settling, washed with water and distilled. Other acid catalysts having a weaker isomerizing action have also been proposed (for example, HF , $\text{HF} \cdot \text{BF}_3$, $\text{H}_3\text{PO}_4 \cdot \text{BF}_3$).

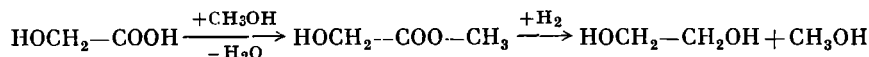
Apart from the synthesis of neoacids from olefins, the acid catalysis of the reactions of carbon monoxide is also employed for the production of α -hydroxy acids from aldehydes:



The reaction is carried out in the liquid phase by bubbling carbon monoxide through a mixture of aldehyde, water and an α -hydroxy acid. Sulphuric acid in an amount of ≈ 3 mol. percent (based on the aldehyde) is dissolved in the liquid and the process is carried out at 200 °C and ≈ 70 MPa. This route is used in the USA on a large industrial scale for the production of *glycolic acid* from formalin:



Glycolic acid serves as an intermediate in the synthesis of ethylene glycol. The acid is esterified by methanol by the ordinary method and the ester is hydrated over a copper-chromite catalyst:

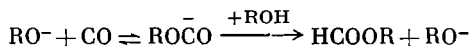


This method of synthesis of ethylene glycol is based on the cheapest hydrocarbon—methane (methane $\rightarrow$ synthesis gas $\rightarrow$ methanol $\rightarrow$ $\rightarrow$ formaldehyde $\rightarrow$ glycolic acid $\rightarrow$ ester $\rightarrow$ ethylene glycol). However, as compared with the ordinary method of production of ethylene glycol via ethylene oxide, this method involves too many steps and has no special advantages.

8.3.3. Base-Catalyzed Processes

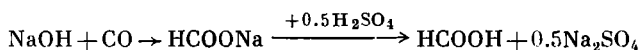
The interaction of carbon monoxide with alcohols catalyzed by the corresponding alkoxide proceeds by way of the attack of this alkoxide on the CO molecule with the intermediate formation of a carbanion, which detaches the proton from the alcohol molecule, regenerating the catalyst and forming the ester of formic acid (for-

mate):

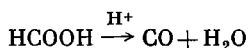


With alkali the same reaction leads to formic acid, which binds the alkali in the form of a salt, which means that a stoichiometric amount of the base is needed.

Formic acid, HCOOH, is one of the important products of basic organic synthesis. It is a liquid (b.p. 100.3 °C) which is miscible with water in all proportions. Formic acid is obtained from sodium hydroxide and carbon monoxide with the subsequent decomposition of sodium formate by the action of sulphuric acid:

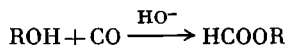


The first step was once carried out with the solid alkali in vessels fitted with scraper mixers. Later, it was found that at 160-200 °C and 1.2-1.5 MPa carbon monoxide reacts well with 25-30-percent alkali in simpler vessels of the bubble-cap type. The resulting solution of sodium formate is evaporated and the dry salt isolated. The second stage—the conversion of the salt to formic acid—is complicated by the possibility of decomposition of formic acid under the action of concentrated sulphuric acid:



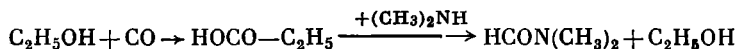
The use of weak sulphuric acid leads to the formation of too strongly dilute formic acid. The solution has been found in the decomposition of the suspension of sodium formate in formic acid. Sulphuric acid is added gradually to the mixture upon vigorous stirring and cooling.

The most economical route to esters of formic acid (formates) is their synthesis from carbon monoxide and alcohols in the presence of bases as the catalysts rather than the esterification of the acid by alcohols:



In this case, there is required only a catalytic amount of alkali, which is why some other derivatives of formic acid can be produced more economically from its esters. *Methyl* and *ethyl formates* are produced at 90-110 °C and ≈ 3 MPa by bubbling carbon monoxide through the alcohol containing 1-2 percent of the alkoxide or alkali.

It is known that the reaction of formates with dimethylamine gives dimethylformamide. It has been suggested that this synthesis be carried out in a single step by treating dimethylamine with carbon monoxide in the presence of a small amount of alcohol and its alkoxide:

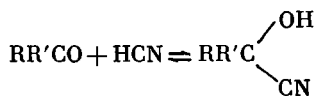


CONDENSATION AT THE CARBONYL GROUP

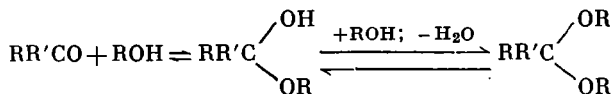
The processes of addition and condensation at the carbonyl group occupy a very important place in the industry of basic organic and petrochemical synthesis. Because of the availability of many aldehydes and ketones and of their high reactivity this method can be used to synthesize monomers and starting compounds for the manufacture of polymeric materials (diphenylolpropane, pentaerythritol and other polyhydric alcohols, isoprene, caprolactam), intermediate products of organic synthesis (higher alcohols, aldehydes and ketones), solvents (oxolanes, isobutyl methyl ketone) and many other valuable products.

The scale of the synthesis of some of the products listed above can be judged by the breakdown of their annual production in the USA (the forecast for 1980): more than 500,000 tons of caprolactam, about 400,000 tons of 2-ethylhexanol, 150,000 tons of diphenylolpropane, about 70,000 tons of pentaerythritol, more than 100,000 tons of isobutyl methyl ketone, etc.

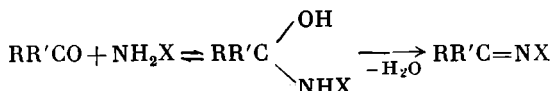
Depending on the conditions, the interaction of aldehydes and ketones with various compounds may stop at the stage of addition of these compounds across the carbonyl group,



may be accompanied by further condensation with a second molecule of the reagent and by the elimination of water, as, for example, in the formation of acetals:

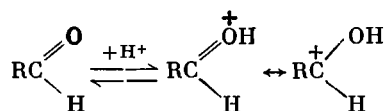


or may be completed by the intramolecular dehydration, which is especially characteristic of reactions with nitrogen bases:



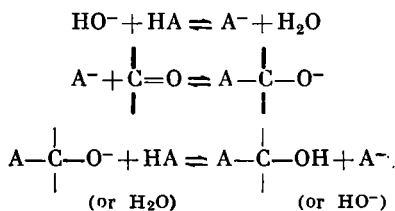
The most important of these processes may be classified as belonging to two principal groups.

1. Reactions of aldehydes and ketones with bases in the broad sense of the term; they include compounds with unshared electron pairs on a heteroatom (nitrogen bases, alcohols) and with π -electron systems (olefins, aromatic compounds). In this case, the activation of the carbonyl group is most often achieved with the aid of protic acids (sulphuric and hydrochloric acids). They protonate the oxygen atom of the carbonyl group, causing the appearance of a partially positive charge on the carbon atom and leading eventually to the formation of a carbonium ion:

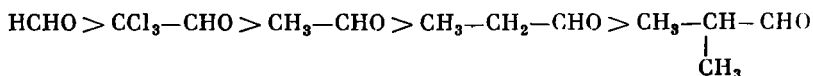


The carbonium ion can attack directly another molecule that has an excess electron density; this is responsible for the condensation of carbonyl compounds with aromatic compounds, olefins, etc.

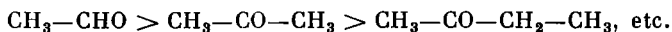
2. Reactions of aldehydes and ketones with weak acids (HCN) and pseudoacids (carbonyl and nitro and other compounds with an activated hydrogen atom), i.e., aldol condensation reactions in the broad sense of the term. These conversions are typically catalyzed by alkalis and bases in general, which convert the acid reagent to its conjugate base, which becomes a strong nucleophile capable of directly attacking the carbonyl carbon:



The reactivity of carbonyl compounds in all the conversions mentioned above depends on the degree of polarization of the carbonyl group, i.e., on the magnitude of the partial positive charge on the carbon atom. Since alkyl groups exert a positive inductive effect, they neutralize this charge to a certain extent. Hence, for aldehydes an increase in the length and branching of the alkyl group leads to a decrease in reactivity and the introduction of chlorine atoms into it causes an increase in reactivity:



The reactivity of ketones is much lower because of the inductive effect of two alkyl groups:

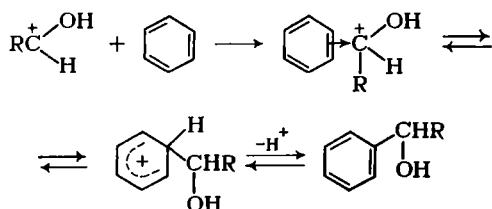


The result and reaction conditions depend in the long run on the activity of the component that attack the carbonyl group.

All condensation reactions at the carbonyl group are exothermic but according to the magnitude of the heat effect they may be divided into two large groups. The first group includes strongly exothermic and practically irreversible reactions of the condensation of carbonyl compounds with aromatics and olefins (the heat effect is 104–106 kJ/mol or 25–35 kcal/mol). The second group includes the reversible processes of formation of acetals and cyanohydrins, aldol condensations proper and reactions with nitrogen bases. The addition step in these reversible reactions has a relatively low heat effect (21–63 kJ/mol or 5–15 kcal/mol), but because of the subsequent condensation or dehydration it may vary considerably in either direction, determining the equilibrium characteristics of the overall process. Usually, the equilibrium is strongly shifted to the right: the addition step is followed by dehydration or relatively stable compounds with five- or six-membered rings are formed.

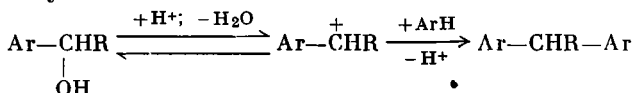
9.1. Condensation of Aldehydes and Ketones with Aromatic Compounds

The reactions of aldehydes and ketones with aromatic compounds are similar in many respects to alkylation processes and also belong to the category of electrophilic substitution reactions. The typical catalysts used are protic acids (sulphuric acids, hydrogen chloride, cation-exchange resins), which convert carbonyl compounds to a positively charged ion, which then attacks the aromatic ring through the intermediate formation of π - and σ -complexes:

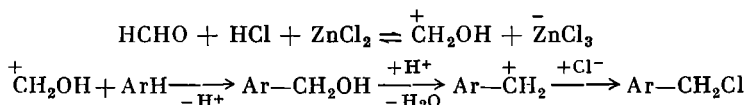


The aromatic alcohol formed reacts further under the conditions of acid catalysis by the mechanism of the alkylation by alcohols and

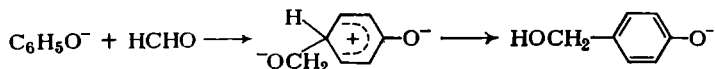
gives a diarylalkane:



The use of aprotic acids as the catalysts is less effective since they decompose by the action of the water liberated. However, for chloromethylation use is sometimes made of a protic acid (HCl) in conjunction with zinc chloride, which increases the acidity of the system:



The reactivity of carbonyl and aromatic compounds varies in the processes under consideration in an ordinary manner. Halogenobenzenes are capable of undergoing these conversions, but aromatic compounds with more electronegative groups do not enter into the reaction. On the contrary phenol interacts with reactive aldehydes (especially with formaldehyde) not only on acid catalysis but also on alkaline catalysis, which is accounted for by the conversion of phenol to a more active form of the phenoxide capable of direct interaction with the aldehyde:

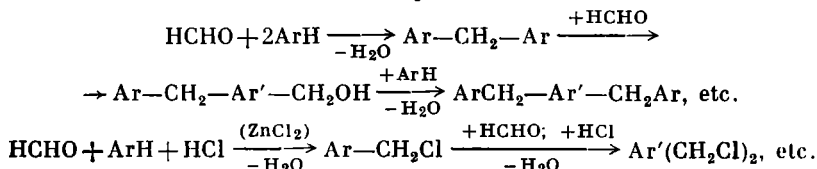


Such reactions form the basis of the production of phenolaldehyde polymers.

The kinetics of these reactions catalyzed by acids satisfies the equation $r = k a_{\text{H}^+} [\text{ArH}] [\text{RCHO}]$, which shows that the slowest step is the interaction of a proton-activated aldehyde molecule with an aromatic compound.

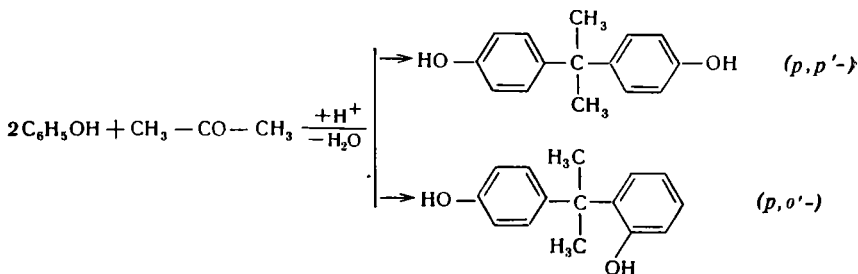
The orientation of the entering group is the same as in other processes of electrophilic substitution in the ring: the reactions with chlorobenzene, phenol and alkylbenzenes yield chiefly *para*-isomers with a small amount of the *ortho*-substituted compound.

The by-products of the condensation of carbonyl compounds with aromatics are always di- and polysubstituted (nuclear substituted) compounds, since the initially formed compounds are capable of further interaction with an aldehyde or ketone:



The formation of these compounds can be reduced by using an excess of an aromatic compound with respect to the stoichiometric amount.

Production of Diphenylolpropane. *Diphenylolpropane* (*bisphenol A*) is a mixture of *p*, *p'*-, *p*, *o'*- and a small amount of *o*, *o'*-bis-2,2-hydroxyphenylpropanes. It is used for the production of polycarbonates and epoxy resins and in a lesser amount for the production of phenol-formaldehyde varnishes. It is obtained by the condensation of phenol with acetone in the presence of acid catalysts:



The reaction involves the formation of numerous by-products: mesityl oxide, $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CO}-\text{CH}_3$ (due to the condensation of acetone); isopropenylphenol, $\text{HO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)=\text{CH}_2$ (the dehydration product of the initially formed hydroxy derivative), polyhydric phenols—the products of the condensation and cyclization of mesityl oxide and isopropenylphenol with phenol, isomers of diphenylolpropane, etc. Most of these compounds are the products of successive conversions, which is why the high yield of diphenylolpropane is favoured by the use of an excess of phenol with its molar ratio to acetone ranging from 3 : 1 to 10 : 1.

The synthesis of diphenylolpropane was originally carried out at 30–40 °C with 70–76-percent sulphuric acid as the catalyst with thioglycolic acid as the promoter. Because of the necessity to use an excess of sulphuric acid (it is diluted by the water liberated) and to regenerate it, and also of the side sulphonation of phenols and the formation of a large amount of toxic sewage this method is not in much favour.

The catalyst that has found wide application is anhydrous hydrogen chloride in the presence of promoters (apart from thioglycolic acid, use may be made of mercaptans and H_2S). The synthesis is carried out at 50–60 °C; the mixture of phenol and acetone is saturated with anhydrous hydrogen chloride, which is introduced together with the promoter. This method has many advantages over the sulphuric-acid process, but in this case too the material of the apparatus undergoes considerable corrosion and acidic waste waters are formed.

The recent development is to use sulpho cation-exchangers as the catalysts; the activity of these catalysts increases when they are

preliminarily dried, just as in other similar cases. The yield of diphenylolpropane increases with increasing molar ratio of phenol to acetone (from 1 : 1 to 5 : 1), with increasing temperature (from 60 to 90 °C) and contact time (from 0.5 to 3 hours), but the increase of the last two parameters leads to an increase in the yield of by-products and to a decrease in the process selectivity. Just as with catalysis by H_2SO_4 and HCl , the activity of the cation-exchanger is substantially influenced by promoters. It has been suggested that

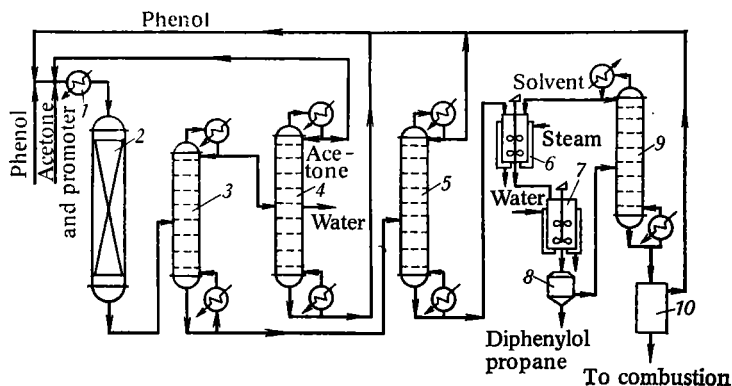


Fig. 9.1. Flow diagram of diphenylolpropane production:

1—steam heater; 2—reactor; 3, 4, 5, 9—fractionating columns; 6—dissolution unit; 7—crystallizer; 8—centrifuge; 10—residue-treatment unit.

mercapto groups be introduced into the sulpho cation-exchanger or a small amount of mercaptans be added to the feedstock.

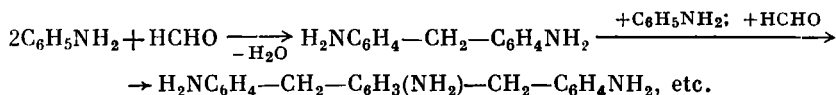
The flow diagram of diphenylolpropane production over a sulpho cation-exchanger is shown in Fig. 9.1. Phenol and acetone (in a molar ratio of 5 : 1) are mixed with a mercaptan and heated in steam heater 1 to 75 °C. The mixture is passed to the upper part of reactor 2, which is a column filled with the cation-exchanger. The reagents are fed at such a rate that the residence time of the liquid in the reactor is 1 hour. The resultant mass is run to fractionating column 3, where the light fraction containing the promoter, unconverted acetone, water and part of phenol is distilled off. The acetone (plus the promoter) and water are distilled off from this fraction in a system of fractionators 4 (only one is shown in Fig. 9.1), the phenol being left in the still. The water is withdrawn for purification and the acetone and phenol are returned to the reaction.

The still residue of column 3 contains phenol, diphenylolpropane and by-products. The phenol is distilled off in vacuum-fractionator 5 and returned to the reactor. The diphenylolpropane is isolated from the remaining mixture by recrystallization from the organic solvent.

To this end, the mixture is dissolved and crystallized on cooling, the precipitated diphenylolpropane crystals being separated on centrifuge 8.

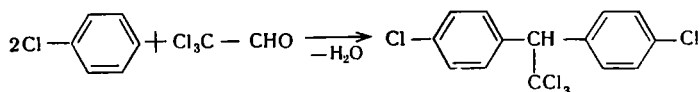
The solvent is regenerated from the mother liquor in fractionation 9 and recycled to the recrystallization stage. The residue from the regeneration of the solvent still contains a considerable amount of diphenylolpropane and by-products (isopropenylphenol), which are capable of forming diphenylolpropane. Therefore, part of the residue is subjected to additional treatment in unit 10 and returned to synthesis; the heavy impurities are burned. The yield of diphenylolpropane reaches 90 percent.

Production of Diaminodiphenylmethanes. The condensation of formaldehyde with aniline leads to the successive formation of many products:



The composition of the mixture depends on the ratio of formaldehyde to aniline. The reaction is carried out by heating formalin with aniline; the resultant mixture consists mainly of diaminodiphenylmethane and triamine. It is used for the production of di- and triisocyanates (page 244).

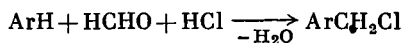
Production of DDT. This compound, which is dichlorodiphenyltrichloroethane by structure, is produced by the condensation of chlorobenzene with chloral on catalysis by concentrated sulphuric acid (oleum):



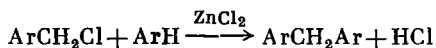
The 4,4'-isomer shown above is a colourless crystalline solid, which melts at 108.5-109 °C. In the technical product it is contained in an amount of 70-75 percent with an impurity of the 2,4'-isomer (20 percent) and the 2,2'-isomer. Commercial DDT is slightly coloured and has a lower melting point. Upon heating to 180-200 °C it decomposes, splitting off hydrogen chloride. DDT has long been the principal insecticide widely used in the home and in agriculture against harmful insects. Today, its use is limited because of the rather high toxicity, the ability to be retained for a long time on tilled land and to be stored in the bodies of animals and birds and in man. In many countries, including the USSR, its application is banned.

The Chloromethylation Reaction. The introduction of the chloromethyl group into the aromatic ring is achieved by the action of

formalin (or paraformaldehyde) and hydrochloric acid on an aromatic hydrocarbon:



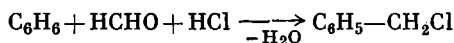
Chloromethylation was carried out until recently in the presence of zinc chloride and sometimes tin tetrachloride. These catalysts are still used at present for less reactive compounds or in special cases. But they cause a side reaction—the condensation of the chloromethylated compound with the feedstock, this leading to the formation of diarylmethanes:



This limits the choice of the temperature, which must not exceed 50–60 °C when zinc chloride is used as the catalyst.

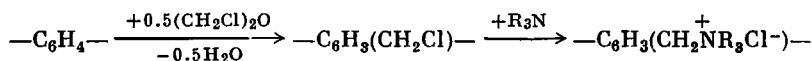
It has been recently found that the chloromethylation of more reactive benzene homologues occurs in the absence of aprotic acids and the catalyst is the reagent itself—hydrogen chloride (or hydrochloric acid). In this case, the temperature must be raised to 90–140 °C and the process carried out under pressure, which is required in order to maintain the liquid state of the reaction mass. No by-product diarylmethanes are formed, since protic acids do not catalyze the condensation of chloro derivatives with aromatic compounds. The process becomes much more economical because the yield of the end product is increased and there is no need for the use of an additional catalyst.

The chloromethylation of benzene in the presence of hydrochloric acid solution of ZnCl_2 is a commercial process for the production of *benzyl chloride*:



but this method is less economical than the chlorination of toluene (page 118).

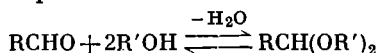
The chloromethylation reaction is used for the production of anion-exchange resins. To this end, the chloromethyl group is introduced into a cross-linked polymer containing aromatic rings and then a quaternary ammonium group is substituted for the chlorine atom:



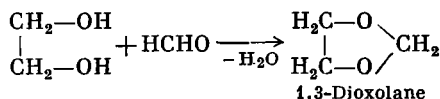
9.2. Synthesis of Acetals and the Prins Reaction. Production of Isoprene

9.2.1. Synthesis of Acetals

Hemi-acetals, $\text{RCH}(\text{OH})\text{OR}'$, and *acetals*, $\text{RCH}(\text{OR}')_2$, are often formed in the synthesis of aldehydes and their various conversions. They are obtained, for example, when alcohols react with aldehydes in the presence of HCl , H_2SO_4 or acid salts of these acids by a reversible reaction, the equilibrium of which is shifted on heating to the side of acetal decomposition:

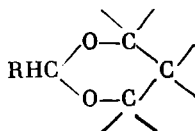


The cyclic acetals of 1,2-glycols—*1,3-dioxolanes*—are much more stable:

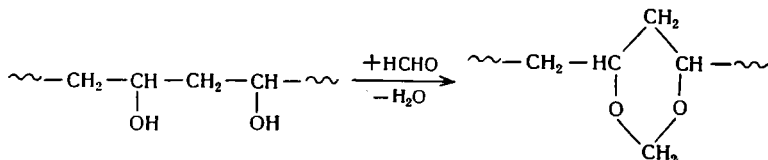


They are produced on an industrial scale since they are good solvents for cellulose esters.

The cyclic acetals of 1,3-glycols are *1,3-dioxanes*:



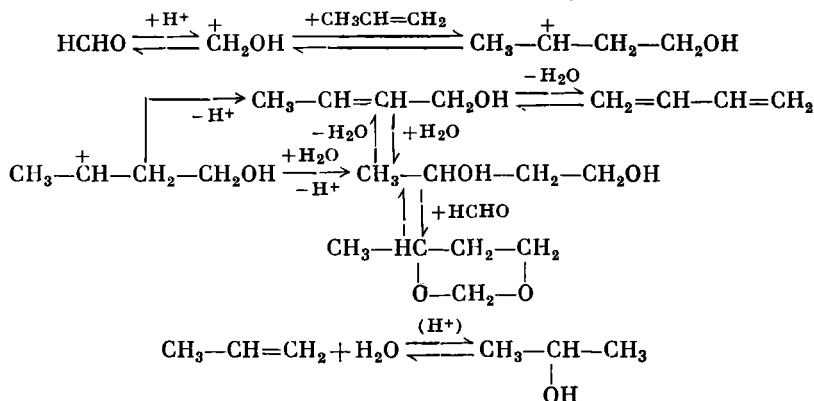
1,3-Dioxane rings are contained in *polyvinyl acetals*, which are an important class of polymers—the derivatives of polyvinyl alcohol. They are obtained by treatment of polyvinyl alcohol with formaldehyde or *n*-butyraldehyde at 60–80 °C in the presence of a phosphoric acid catalyst:



9.2.2. The Prins Reaction

The condensation of aldehydes with olefins, which proceeds in the presence of an acid-type catalyst (the Prins reaction), has assumed commercial significance for the synthesis of a number of com-

pounds. Depending on the reaction conditions, the dominant products are the derivatives of 1,3-dioxane or 1,3-glycols. Besides, the reaction gives rise to by-products—unsaturated monohydric alcohols, saturated alcohols (the hydration products of starting olefins) and more complex oxygenated compounds. As the temperature is raised there may also occur the dehydration of the glycol and unsaturated alcohol with the formation of a diene. The formation of all these compounds is well illustrated by the following scheme:



1,3-Dioxanes are the dominant condensation products at moderate temperatures (up to 90-100 °C) and with an excess of formaldehyde with respect to the olefin. The formation of 1,3-glycol is favoured by a deficiency of formaldehyde and an increase in temperature. This is accompanied by the increased formation of by-product unsaturated alcohols; at an even higher temperature dienes are also formed as by-products.

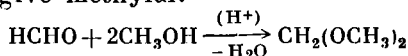
The reactivity of olefins varies in the same way as in other electrophilic reactions. Ethylene enters into condensation with much difficulty; isobutylene reacts most readily and a temperature of 25-40 °C is sufficient for it at a 10-30-percent concentration of sulphuric acid (the catalyst). However, in order to intensify the process and to reduce the amount of acid consumed, a higher temperature (70-90 °C) is maintained under industrial conditions and the concentration of sulphuric acid is accordingly lowered to 1.5 percent. For other olefins more severe conditions are required (for example, 100-115 °C and 3-5-percent H_2SO_4 for propylene). The reaction conditions are even more severe in going from formaldehyde to less reactive acetaldehyde and to their higher homologues. Apart from sulphuric acid, other catalysts have also been proposed for the reaction: hydrogen chloride, phosphoric and phosphomolybdic acids, zinc chloride, boron fluoride, etc., but only sulphuric acid has assumed industrial importance.

9.2.3. Production of Isoprene

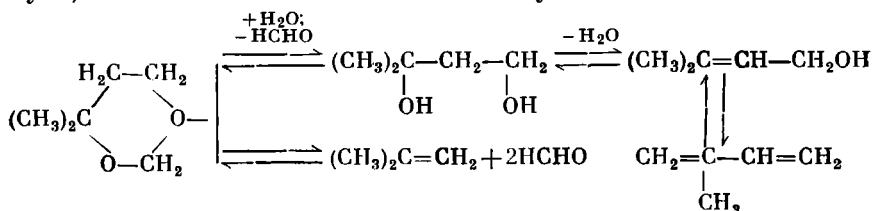
1,3-Dioxanes and 1,3-glycols obtained by the Prins reaction are of some value as solvents and intermediates for the synthesis of plasticizers, emulsifying agents, etc. But the Prins reaction has assumed its main industrial significance in the production of isoprene. The technology of isoprene production was first developed in the USSR by M. I. Farberov and M. S. Nemtsov. At present, isoprene is produced by this route in many other countries as well.

The *first step* is the condensation of isobutylene with formaldehyde in the presence of sulphuric acid as the catalyst (1-1.5 percent by weight based on isobutylene). The molar ratio of C_4H_8 to $HCHO$ in the starting mixture is 0.73 : 1; the reaction mass must always contain free formaldehyde in order to prevent the polymerization of isobutylene. Isobutylene may be used either pure or mixed with butanes; it may contain *n*-butylenes, which are less reactive and remain unchanged. Formaldehyde is used in the form of a 37-percent aqueous solution (formalin), which is diluted with the recycle before being fed into the reactor. The process is carried out at 85-95 °C and 1.5-2 MPa, when all the reagents are in the liquid state. Thus, the reaction mass is a liquid two-phase system and the intensity of the reaction depends considerably on the degree of interfacial contact. The degree of conversion of isobutylene and formaldehyde in the reaction is usually 85-90 percent.

The major products under these conditions are 4,4-dimethyl-1,3-dioxane (the selectivity is 66-68 percent with respect to isobutylene and 80-83 percent with respect to formaldehyde), *tert*-butyl alcohol (the yield is about 15 percent based on isobutylene) and 3-methyl-1,3-butanediol (5-7.5 percent). Besides, the reaction gives rise to isomeric unsaturated alcohols and 5-methyl-5,6-dihydropyran formed by way of ring closure. Since methanol is contained in formalin, it is also present in the reaction mass and reacts partially with formaldehyde to give methylal:



The *second step* consists of the catalytic hydrolysis and dehydration of 4,4-dimethyl-1,3-dioxane to isoprene. This is accompanied by the side reaction of its decomposition to isobutylene and formaldehyde, which is the reverse of dioxane synthesis:



The other products of the first step (unsaturated alcohols and diol) can also be converted to isoprene, which is why it is expedient to dehydrate them together with dioxane in order to increase the overall yield of isoprene.

Various heterogeneous acid catalysts have been proposed for the second step of the process (supported phosphoric acid, phosphates,

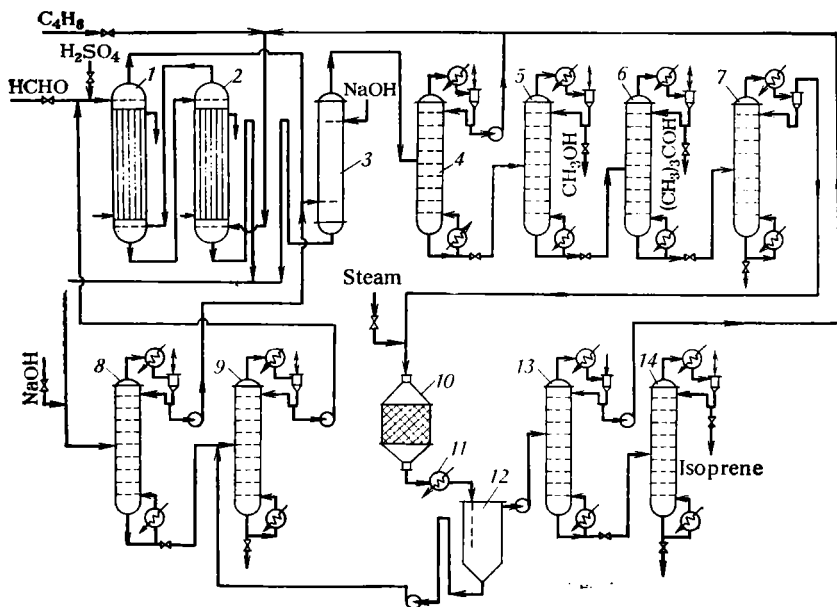


Fig. 9.2. Flow diagram of production of isoprene from isobutylene and formaldehyde:

1, 2—reactors; 3—neutralizer; 4, 5, 6, 7, 8, 9, 13, 14—fractionating columns; 10—reactor; 11—cooler; 12—separator.

silica gel, etc.); the reaction is carried out in the gas phase at 250–400 °C. In order to compensate for the endothermicity of the reaction the dioxane is diluted with superheated steam, which serves as a heat-retaining medium and also favours the increase of the reaction selectivity. The degree of conversion of dioxane at this step is ≈ 90 percent with a selectivity to isoprene being 83–84 percent (the remainder is mainly isobutylene, a small amount of methylbutyraldehyde and other high-boiling compounds).

Technology of Two-Step Synthesis of Isoprene. A simplified flow diagram of isoprene production from the isobutylene fraction and formaldehyde is given in Fig. 9.2. The first step is carried out in tubular reactors 1 and 2 which are cooled by water. The isobutylene

fraction and the aqueous solution of formaldehyde diluted with the recycle move countercurrently in these reactors: the heavier aqueous layer flows downwards and the light hydrocarbon layer moves upwards; the dispersion of the liquids provides a large interface for contact of the two phases. The upper and lower parts of these reactors operate as separators, in which the hydrocarbon and the aqueous layer are separated, respectively. The dioxane and unsaturated alcohols almost completely pass over into the hydrocarbon layer, the unconverted formaldehyde, part of methanol and diol being left in the aqueous layer.

The aqueous layer from the lower part of reactor 2 is neutralized by caustic and in column 8 all the volatile compounds are distilled off from it and combined with the hydrocarbon layer. Then, in column 9 the dilute aqueous solution of formaldehyde is distilled off from the still bottoms of column 8 and the recycle formalin from the second step of the process and then separated from the heavy residues. This solution is returned to the reaction with fresh formalin added to it.

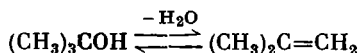
The hydrocarbon layer from the top of reactor 1 and the light fraction from the fractionation of the aqueous layer are combined and treated in neutralizer 3 with the countercurrently flowing aqueous solution of alkali, which is then mixed with the aqueous solution emerging from reactor 2; the mixture is sent for joint processing described above. The unconverted isobutylene is distilled off from the scrubbed hydrocarbon layer in column 4 and returned to the reaction (when the fraction containing butanes and *n*-butylenes is used, an additional fractionation is required for "strengthening" the isobutylene in order to prevent their buildup in the recycle). Then, in column 5 more volatile methanol and methylal are distilled off from the reaction products, and in column 6 *tert*-butyl alcohol distills out. The dioxane (together with unsaturated alcohols) is separated in column 7 from the heavier residue and led to the second step of the process.

The dioxane vapours are diluted with superheated steam and the resultant mixture is run into adiabatic-type reactor 10 carrying a fixed bed of a heterogeneous catalyst. The reaction mixture is condensed in cooler 11 and the organic layer is separated from the aqueous layer in separator 12. The aqueous layer, which contains formaldehyde, is transferred to column 9 where it is processed together with the aqueous solutions obtained after the first step.

The organic layer from the top of separator 12 is led successively to two fractionating columns. The isobutylene formed in the decomposition of dioxane is distilled in the first column (13) and returned to the first synthesis stage. Then, isoprene is separated in column 14 from the higher-boiling residue (the unconverted dioxane and by-products). The final purification is achieved as follows: the isoprene

is washed with water, dried by azeotropic distillation and subjected to final fractionation. At these stages an inhibitor is added to it to prevent its polymerization.

One-Step Synthesis of Isoprene. The interaction of isobutylene with formaldehyde (the Prins reaction) at a higher temperature in the liquid phase involves a gradual decomposition of 4,4-dimethyl 1,3-dioxane, unsaturated alcohols and diol with the formation of isoprene. This is seen from Fig. 9.3, which shows the time dependence of the yield of the products at 160 °C. This has been used as the basis for the development of a single-step synthesis of isoprene in the liquid phase at 150-160 °C and ≈ 3 MPa in the presence of water-soluble Lewis acids as the catalysts. Apart from the smaller number of vessels and the reduction in the capital cost, the problem of utilization of by-products is solved better in the one-step synthesis; the by-products include *tert*-butyl alcohol, which may be returned to reaction, in which it is in equilibrium with isobutylene:



The use of *tert*-butyl alcohol (obtained in the extraction of isobutylene from the C_4 frac-

tions or in the isobutane variant of propylene epoxidation) has been suggested as the feedstock instead of isobutylene.

Another variant of the single-step synthesis of isoprene consists of the heterogeneous-catalytic reaction in the gas phase at 200-350 °C. It is claimed to have high selectivity (up to 80 percent based on formaldehyde and 90 percent on isobutylene) with the corrosion of the material of the apparatus being reduced and the quality of the product (isoprene) being improved.

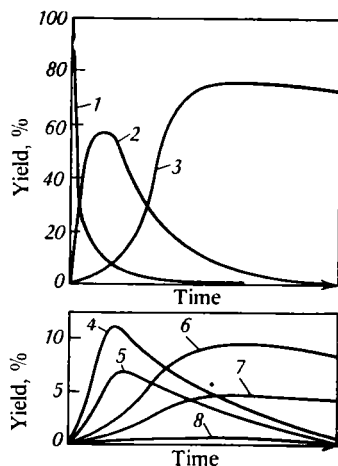


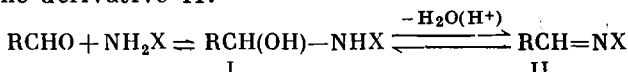
Fig. 9.3. Dependence of the yield of the products of the reaction of formaldehyde with isobutylene on the reaction time:

1—formaldehyde; 2—4,4-dimethyl-1,3-dioxane; 3— isoprene; 4—3-methyl-3-buten-1-ol; 5—3-methylbut-en-2-ol; 6—5-methyldehydro-5,6-pyran; 7—*tert*-butyl methyl ether; 8—3-methylbutan-1,3-diol.

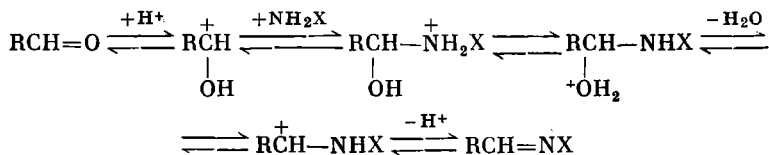
9.3. Condensation of Aldehydes and Ketones with Nitrogen Bases.

Production of Caprolactam

The interaction of aldehydes and ketones with nitrogen bases (ammonia, amines, hydroxylamine), which are designated here as NH_2X , involves at least two steps. The first step is the addition at the carbonyl group with the formation of an alkylol derivative I; the second step is the dehydration of the alkylol derivative to an azomethine derivative II:



With highly reactive formaldehyde the first step does not require a catalyst, but the second step, like other dehydration reactions, is effectively accelerated by catalysts, which simultaneously catalyze the first step:



An acid catalyst has also a negative effect, converting part of the nitrogen base to a salt which fails to react with the carbonyl

compound because of the saturation of the unshared electron pair on the nitrogen atom. For this reason, the dependence of the reaction velocity on the strength and concentration of the acid-catalyst is found to be rather complicated. Usually, the reaction velocity first increases with increasing acidity of the medium, but at a certain pH, characteristic of each nitrogen base, it reaches a maximum and then falls off (Fig. 9.4). The maximum on the kinetic curve is shifted to the right (i.e., to the region of lower acidity) the more strongly, the stronger is the nitrogen base.

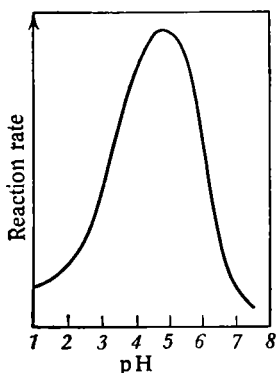
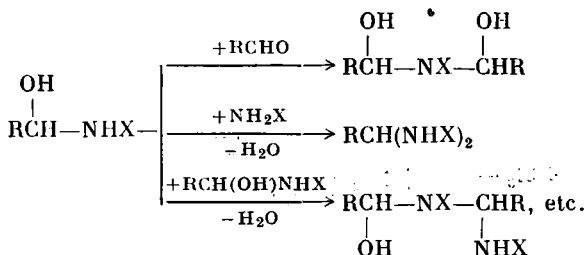


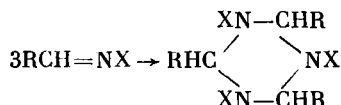
Fig. 9.4. Dependence of the rate of the reaction of acetone with hydroxylamine on the pH of the medium.

The interaction of carbonyl compounds with nitrogen bases is not limited to the steps considered above. Depending on the reaction

conditions used, the addition products formed at the first step may undergo condensation with a second aldehyde molecule, with the nitrogen base or they may condense with one another:

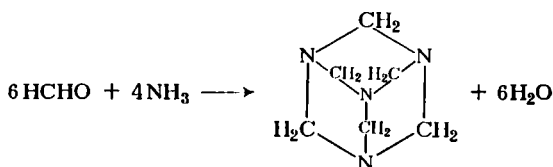


The azomethine derivatives (II) resulting from the dehydration of the alkylol derivatives (I) may in turn undergo polymerization with ring closure:



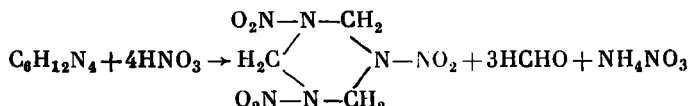
9.3.1. Condensation Products of Aldehydes with Ammonia and Amines

Hexamethylenetetramine (urotropine) is obtained by the condensation of formaldehyde with ammonia:



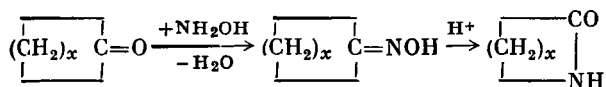
The reaction is carried out without the aid of catalysts; formalin is mixed with an aqueous solution of ammonia on cooling. The resultant solution is clarified with activated carbon and evaporated in vacuum to the paste-like state. The crystalline urotropine obtained after centrifuging and drying is additionally purified and subjected to recrystallization to bring it to the pharmaceutical condition.

Hexamethylenetetramine is used for the production of phenol-aldehyde polymers and also as a curing agent. With nitric acid it forms an explosive, *hexogen*:



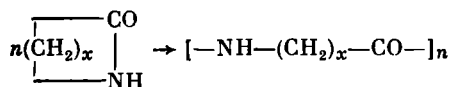
9.3.2. Production of Caprolactam and Other Lactams

The most important industrial application of reactions of condensation of ketones with nitrogen bases is the production of oximes (from cycloalkanones and hydroxylamine), which undergo a Beckmann rearrangement to lactams:



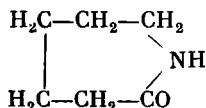
Lactams are the inner (cyclic) amides of amino acids; they are named after the corresponding carboxylic acid: valerolactam (C_5), caprolactam (C_6), enantholactam (C_7), etc.

The polymerization of lactams, which involves the opening of the ring, yields the most popular types of polyamides:



which are named according to the number of carbon atoms in the lactam (nylon 5, nylon 6, etc.) or after the carboxylic acid (capron, polycapramide).

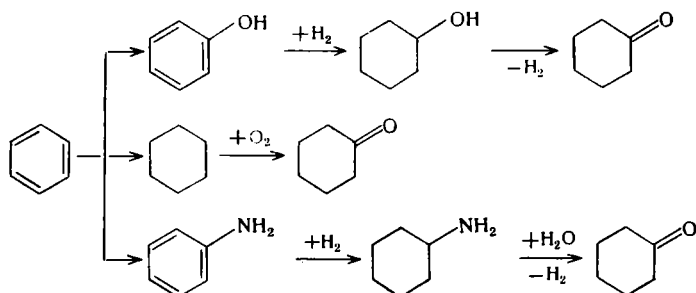
The most important of these compounds is *caprolactam*:



Caprolactam is a colourless crystalline substance (m.p. 70°C ; b.p. 139°C at $\approx 1.6\text{ kPa}$); it is well soluble in water and organic solvents. It is used to produce synthetic fibres (especially nylon 6) which possess excellent physico-mechanical characteristics and which are extensively used for the manufacture of various technical items and consumer goods.

The most important methods of production of caprolactam and other lactams are based on the processing of the corresponding cyclanones by way of their oximation and Beckmann rearrangement and differ only by the method of production of the ketone. For example, in the synthesis of caprolactam, cyclohexanone is obtained

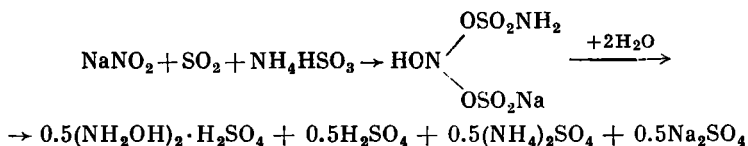
from benzene via phenol, cyclohexane or aniline:



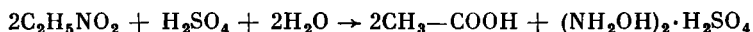
Caprolactam was originally obtained from phenol, but today it is mainly produced from cyclohexane, which reduces the number of steps and capital cost. For example, if the cost of caprolactam obtained from phenol is assumed to be equal to 100, then the figures for caprolactam synthesized from aniline and cyclohexane are 135 and 85, respectively.

The method of production via cycloalkanes is general for lactams; the methods of synthesis of the corresponding cycloalkanones have been described earlier (page 415).

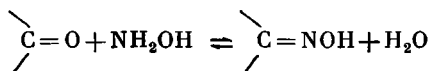
Production of Oximes from Ketones. The step of oxime production from cycloalkanones (the oximation reaction) consists of the treatment of cycloalkanones with hydroxylamine in the presence of acid catalysts. For this reaction, use is made of an aqueous solution of hydroxylamine sulphate containing 4-5 percent of NH₂OH. It is prepared by two principal methods—the reduction of the salts of nitric acid or from nitroalkanes. In the first method, nitrites are reduced by sulphur dioxide and ammonium disulphite:



When oximes are to be obtained from nitroalkanes, nitroethane or any other nitroparaffin is treated with sulphuric acid, which leads to the formation of hydroxylamine sulphate and a carboxylic acid:



The oximation reaction itself is reversible:



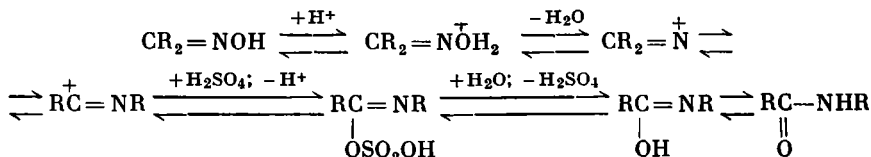
Because of the high basicity of hydroxylamine the equilibrium of the oximation reaction is shifted to the right with decreasing acidity of the medium. The acidity of the medium has also an effect on the reaction velocity, which passes through a maximum at $\text{pH} = 4.5$. Because of the high rate of the chemical reaction and the heterogeneity of the process it is influenced by the diffusional factors, which requires an intensive stirring of the mixture. A more complete conversion of the ketone is achieved by using an excess of hydroxylamine (≈ 5 percent).

The principal side reaction involved in oximation is the formation of the product of self-condensation of 2-cyclohexanone—cyclohexylidenecyclohexanone. Its yield increases with increase of temperature, cyclohexanone concentration and acidity of the medium. For this reason and also in order to achieve a more complete conversion of the reagents the oximation reaction is carried out in two steps. At the first step, use is made of an excess of cyclohexanone with respect to hydroxylamine and a temperature of $\approx 40^\circ\text{C}$ is maintained in order to avoid the side condensation of the ketone. The second stage involves the oximation of the remaining cyclohexanone in the presence of excess hydroxylamine, when the temperature is raised to $75\text{--}80^\circ\text{C}$, which is sufficient for the prevention of the crystallization of the crude oxime (the crystallization temperature of this compound in pure form is 88.6°C). The yield of the oxime under the conditions indicated is 99 percent.

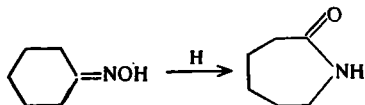
Other oximes of cycloalkanones are produced in an analogous way.

Beckmann Rearrangement of Oximes to Lactams. The Beckmann rearrangement of oximes to substituted amides of acids proceeds in the presence of strong mineral acids, of which oleum found widest application.

The mechanism of the Beckmann rearrangement is ionic and involves the intermediate formation of a cation with a positive charge on nitrogen, to which the alkyl group migrates:



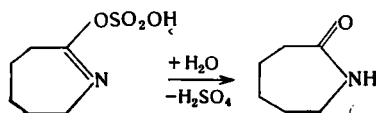
In the case of cycloalkanones the same rearrangement of their oximes leads to lactams, say, to the formation of caprolactam from cyclohexanone oxime:



The reaction is strongly exothermic ($-\Delta H^\circ = 235 \text{ kJ/mol}$) and its rate increases with increasing acidity and temperature. With acids containing water there occurs an undesirable process—the hydrolysis of oximes to ketones and of lactams to amino acids. In this process, water (4-5 percent) is introduced into the mixture with the crude oxime; this requires the use of 20-percent oleum in such an amount as to bring the content of excess SO_3 to about 1.5 percent in the rearranged product. For the consumption of oleum to be reduced it has been suggested that the oxime be dried or the oximation be carried out in an organic solvent, in which case the anhydrous product is subjected to rearrangement.

The Beckmann rearrangement is carried out at $\approx 125^\circ\text{C}$, when the process occurs very rapidly and may be accompanied by the ejection of the reaction mixture. This can be prevented by carrying out the reaction in a flow-circulation system with the mixture being intensively stirred and cooled.

After the rearranged mass consisting of the sulphate of the enol form of lactams is neutralized a lactam is obtained:



Production of Caprolactam. The flow diagram of caprolactam production from cyclohexanone is given in a simplified form in Fig. 9.5.

Cyclohexanone is continuously charged into reactor 1 of the first stage of oximation, where at 40°C it interacts with a solution of hydroxylamine sulphate in aqueous ammonium sulphate obtained at the second stage of oximation. The reaction mass overflows into separator 2, where the aqueous solution of ammonium sulphate is separated from the cyclohexanone containing the oxime obtained in reactor 1. Cyclohexanone is sparingly soluble in water and the oxime dissolves better. Though the solubility of the latter in concentrated aqueous ammonium sulphate decreases, it is still considerable. Because of this, the treatment of fresh cyclohexanone with partially spent hydroxylamine sulphate has a further advantage: the excess of the ketone extracts the oxime from the aqueous-sulphate layer, the loss of the oxime with ammonium sulphate being reduced. This is supplemented by the extraction of the oxime from the ammonium sulphate solution leaving separator 2 using cyclohexanone or an organic solvent (not shown in Fig. 9.5).

The cyclohexanone containing the oxime is pumped from the top of separator 2 to the second stage of oximation, which is accomplished at $75\text{--}80^\circ\text{C}$ in a cascade of reactors (3 and 4) fitted with stirrers and

cooling coils. The mixture of cyclohexanone and oxime from the first oximation stage and a fresh solution of hydroxylamine sulphate are introduced into reactor 3. The reaction mass overflows from one reactor to another, ammonia liquor being added to each reactor to control the pH of the medium (as the hydroxylamine, which is more basic than the oxime, is exhausted the acidity of the mixture increases and it is therefore necessary to add ammonia liquor to both reactors).

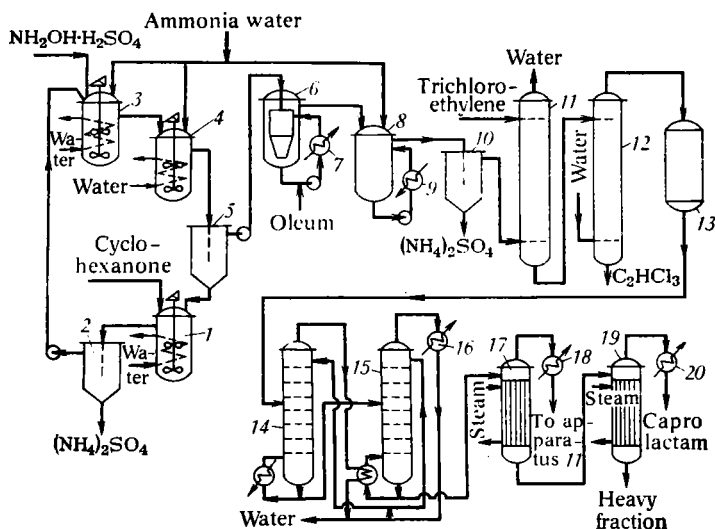


Fig. 9.5. Flow diagram of caprolactam production:

1—reactor for the first stage of oximation; 2, 5, 10—separators; 3, 4—reactors for the second stage of oximation; 6—rearrangement reactor; 7, 9—external coolers; 8—neutralizer; 11, 12—extraction units; 13—purification unit; 14, 15—stripping columns; 16, 18, 20—condensers; 17, 19—film vaporizers.

The mixture which practically contains no ketone leaves the last second-stage reactor. It splits in separator 5 into an aqueous-sulphate layer (containing unconverted hydroxylamine and led to the first oximation stage to reactor 1) and the crude oxime, which contains ≈ 5 percent of water, a small amount of ammonium sulphate, cyclohexanone and by-products. It is run to the rearrangement stage usually without purification.

The Beckmann rearrangement of the oxime is effected in reactor 6 of the cyclone type fitted with a circulation pump and a powerful cooler 7. Oleum is introduced into the circulating mixture prior to the pump; the recycle liquid is fed in the tangential direction of the cyclone located inside the reactor, and the oxime is fed along its axial direction. As a result, conditions are created for intensive stirring of the reagents and for safe operation (no overshooting of

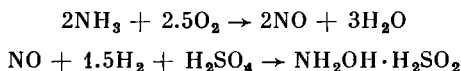
the mixture and overheating are usually observed). The resultant mass overflows through a crossover main into neutralizer 8, into which the required amount of ammonia liquor is introduced. In order to prevent overheatings and the hydrolysis of the resulting lactam the neutralization is carried out at 40-50 °C, this being attained by circulating the mixture through external cooler 9. The neutralized mass overflows into separator 10, where the hydrous ammonium sulphate is separated from the so-called lactam oil. The lactam is soluble in hydrous ammonium sulphate and in order to avoid the loss of the lactam it is additionally extracted from the ammonium sulphate using an organic solvent (not shown in Fig. 9.5).

The resultant lactam oil contains 60-65 percent of lactam, 30-35 percent of water, up to 2 percent of ammonium sulphate and impurities of unconverted reagents and by-products. The task now is to isolate high-purity caprolactam. The first step is the extraction of the lactam by using an organic solvent (benzene, toluene, trichloroethylene) and the re-extraction from the organic solution by water; these operations are effected in rotating-disk extractors. When trichloroethylene is used, it is fed into the upper part of extractor 11 and the lactam oil into the lower part. The water together with the impurities dissolved in it is removed from the top of the vessel, and the organic layer from the bottom of extractor 11 is led to re-extractor 12, where the lactam dissolves in water and is separated from the impurities soluble in trichloroethylene. The trichloroethylene is withdrawn from the bottom of the re-extractor and led to regeneration (not shown in Fig. 9.5).

The aqueous solution of lactam from the top of apparatus 12 is subjected in unit 13 to chemical purification, first with the aid of ion-exchange resins and then by hydrogenation over a heterogeneous catalyst. The purified lactam solution is evaporated (in vacuum) in a cascade of stripping columns (two such columns, 14 and 15, fitted with sieve trays are shown in Fig. 9.5) using the steam of the previous column for heating the boilers of the subsequent columns. Part of the water distilled out is sent to reflux the columns, the remainder being withdrawn from the system. The evaporation gives 95-97-percent lactam. The final purification stage is distillation, which is effected in vacuum rotating-film evaporators in order to prevent the thermal decomposition of the lactam. First, the water that entrains the lactam is distilled off in vaporizer 17. This light fraction is returned to the extraction stage to unit 11 or to unit 8 for neutralization. The lactam from vaporizer 17 passes to vaporizer 19, where pure caprolactam is distilled off from the heavy residue. The latter still contains a considerable amount of caprolactam, which is distilled off in an additional vaporizer and returned to chemical purification unit 13 or to extractor 11 (not shown in Fig. 9.5).

Caprolactam is produced in a yield of 90-95 percent based on cyclohexanone. If the lactam polymerization plant is nearby, caprolactam is transported there in molten form. Otherwise, caprolactam is crystallized.

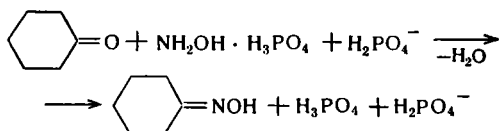
Improvement of the Process. The method of caprolactam production described above has two main disadvantages: the expensive synthesis of hydroxylamine sulphate and the consumption of a large amount of sulphuric acid and ammonia with the formation of 4-5 tons of waste ammonium sulphate (which is of little value) per 1 ton of caprolactam. The major improvement has been the development of a new route to hydroxylamine sulphate—the catalytic hydrogenation of oxides of nitrogen (nitrose gases). They are produced by the oxidation of ammonia, and the hydrogenation is effected in dilute sulphuric acid in the presence of platinum deposited on activated charcoal:



The former method of production of hydroxylamine sulphate is now being replaced everywhere by the new method, which substantially improves the economics of caprolactam production.

Of great interest is the *hydroxylamine-phosphate method* of caprolactam production, which makes it possible to reduce the consumption of sulphuric acid by 60 percent with the formation of only 1.8 ton of ammonium sulphate per 1 ton of product. The essence of the method is that if hydroxylamine phosphate is used for the oxidation step, it is possible to recirculate the phosphate "buffer" for the synthesis of hydroxylamine phosphate, which cannot be done in the traditional sulphate variant.

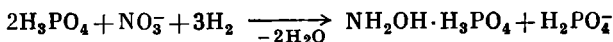
The oxidation occurs at pH from 2 to 1 according to the reaction equation:



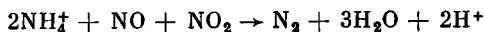
Here, in contrast to the sulphuric-acid medium, the oxime can be extracted from a weakly acidic solution of the phosphate "buffer" without neutralization of the mixture—by extraction with toluene, in the presence of which the oxidation is carried out. The isolated solution of the phosphate "buffer" is treated with nitric acid



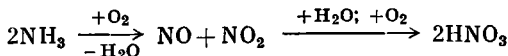
and then hydrogenated by hydrogen in the presence of palladium on activated charcoal to give hydroxylamine phosphate



and the solution is again recycled to oximation. The hydrogenation, however, gives nitrogen and even ammonia (in the form of NH_4^+) as by-products. The latter causes a change in the pH of the phosphate "buffer", which is why an excess of NH_4^+ ions must be removed. This is achieved by treatment of the solution with nitrose gases:



from which there is also obtained nitric acid:



required for the synthesis of hydroxylamine.

The block diagram of the hydroxylamine-phosphate process is shown in Fig. 9.6. It consists of an inorganic and an organic cycle combined in oximation block 4.

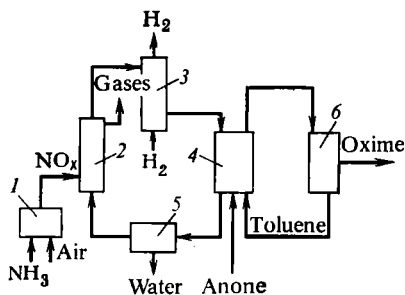


Fig. 9.6. Block diagram of the hydroxylamine-phosphate method of oximation:

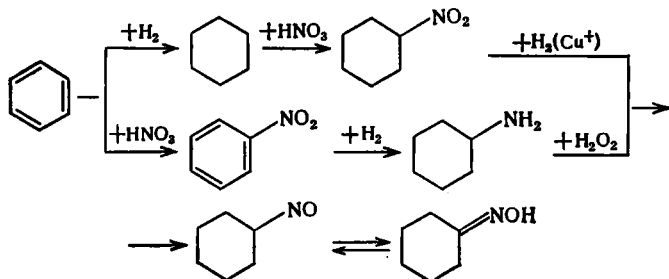
1—ammonia oxidation block; 2—block for absorption of nitrous gases; 3—hydrogenation block; 4—oximation block; 5—stripper; 6—solvent recovery block.

required and ammonium sulphate by-product is formed (the co-production of ammonium sulphate with caprolactam is a nuisance). Complete elimination of by-product ammonium sulphate is possible (and has been realized on a certain scale in the industry) by burning it or by way of cracking with the formation of NH_3 , SO_2 and SO_3 , from which all of the sulphuric acid (oleum) and part of the ammonia are recovered.

Other Methods of Lactam Synthesis. These methods may be divided into two groups, in which (1) an oxime is obtained by a differ-

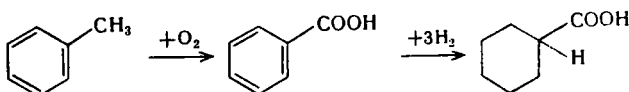
ent route, avoiding the ketone step; (2) a lactam is obtained by a different route, with the ketone and oxime steps being omitted.

The reactions of the first group proceed through the step of nitro compounds, which are isomeric in the aliphatic series to oximes and which are readily rearranged to oximes:

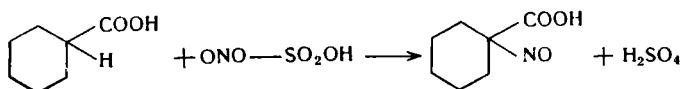


Of the processes of this group, other methods involving a direct nitrosation of organic compounds have become industrially important.

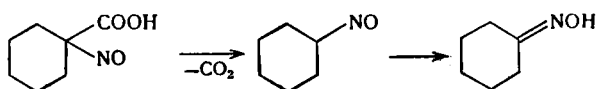
One of these methods is used to produce exclusively caprolactam, with toluene being used as the feedstock instead of benzene (toluene is more available). Toluene is oxidized to benzoic acid, which is hydrogenated to cyclohexanecarboxylic acid:



The cyclohexanecarboxylic acid is then treated with nitrosylsulphuric acid and oleum at 100-140 °C to give directly caprolactam. In the reactions that take place cyclohexanecarboxylic acid undergoes nitrosation across the tertiary carbon atom



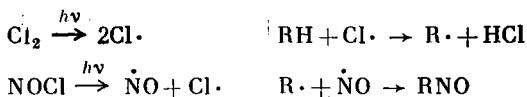
and then the carboxyl group at the quaternary carbon atom is easily eliminated and nitrosocyclohexane is isomerized to the oxime:



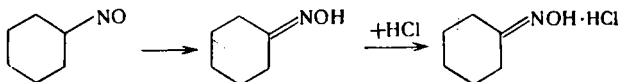
The action of oleum rearranges cyclohexanone oxime to caprolactam, which is produced in a yield of 85-90 percent.

Of greater interest is the method of photochemical nitrosation of cycloalkanes, which can be employed for the production of capro-

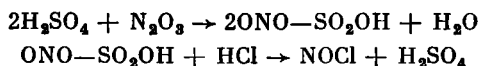
lactam and other lactams. Photochemical nitrosation can be accomplished at 0-30 °C with a mixture of nitrogen oxide with chlorine or nitrosyl chloride, NOCl. When the reaction mass is irradiated, a radical-chain process occurs with the chain being initiated by way of the homolytic scission of the chlorine molecule or of the nitrosyl chloride molecule:



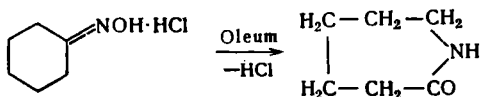
The resultant nitrosylcyclohexane immediately undergoes rearrangement to cyclohexanone oxime, which reacts with hydrogen chloride to give cyclohexanone oxime hydrochloride:



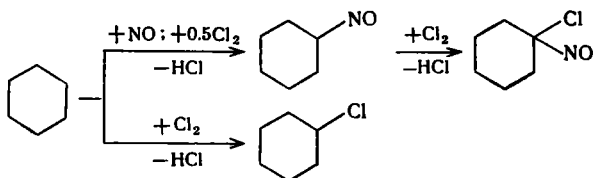
The required nitrosyl chloride is obtained from the gases of ammonia oxidation. The absorption of nitrose gases by sulphuric acid gives rise to nitrosylsulphuric acid, which is acted on by hydrogen chloride to form nitrosyl chloride:



A mixture of gaseous nitrosyl chloride and hydrogen chloride is charged into the reactor equipped with mercury vapour lamps; the gases bubble through liquid cyclohexane. The cyclohexanone oxime hydrochloride is separated directly in the reactor in the form of an oily layer. When it is reacted with oleum, a Beckmann rearrangement to caprolactam takes place:

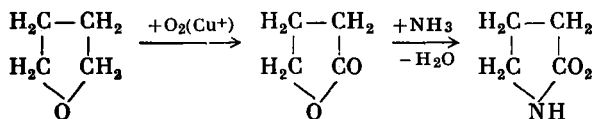


The hydrogen chloride evolved can be re-used for the production of nitrosyl chloride and cyclohexanone oxime hydrochloride. The by-products obtained are chloronitrosocyclohexane and chlorocyclohexane, which are formed as a result of photochemical chlorination:

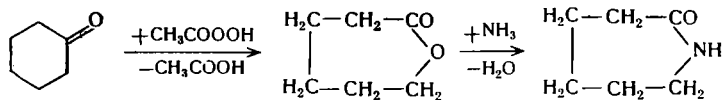


These reactions can be suppressed by using a low temperature and an excess of hydrogen chloride and by removing cyclohexanone oxime hydrochloride as it is formed; when the nitrosation is effected with a mixture of NO and Cl₂, an excess of nitrogen oxide with respect to chlorine (2.5 : 1) must be used. The yield of cyclohexanone oxime is 90-95 percent. Because of the high yield of the end product, the reduced number of process steps and the reduced consumption of sulphuric acid this method, which was first developed in Japan, has become very important and has been commercialized in some countries.

Of the second group of methods used for the synthesis of lactams, in which the steps leading to ketones and oximes are avoided altogether, the amidation of lactones is of greatest interest. For example, butyrolactam (pyrrolidone) is most simply obtained from butyrolactone:



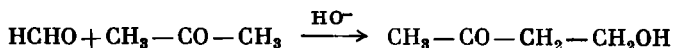
A new synthesis of caprolactam from cyclohexanone via caprolactone has been developed and commercialized:



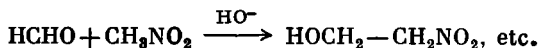
Most of the above-described methods of caprolactam production are not employed in the industry because they have shortcomings. Of the world's total production of caprolactam 78.2 percent is provided by the methods based on the use of cyclohexanone, 16.8 percent by the nitrosation of cyclohexane and 5 percent by the toluene method.

9.4. Reactions of the Aldol Condensation Type

In the broad sense of the term, *aldol condensation* is a reaction in which aldehydes and ketones combine together

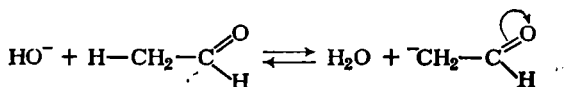


or with compounds that contain a relatively mobile hydrogen atom attached to a carbon atom (with pseudoacids), say with nitro compounds:

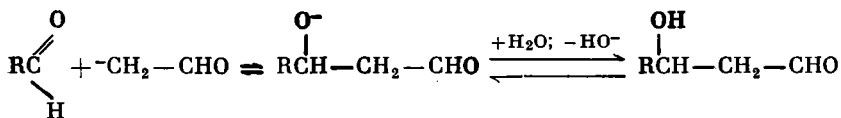


One molecule of the carbonyl compound reacts here across the carbonyl group (the carbonyl component) and the second across the α -methylene group (the methylene component) activated by the carbonyl (or by any other electronegative group).

The role of the base as the catalyst for these reactions consists in that it converts the methylene component to a very reactive anion according to the typical scheme of acid-base equilibrium. The anion can be rendered sufficiently stable by way of conjugation with an electronegative group present in the methylene component:



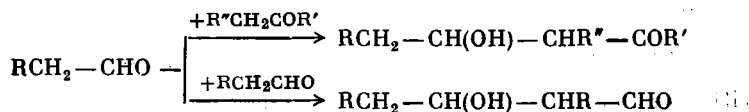
It is because of this that the reaction always proceeds at the α -carbon atom adjacent to an electronegative grouping. The resultant anion is a strong nucleophile and interacts directly with the carbonyl carbon atom of the carbonyl component, following which the intermediate anion with a negative charge on the oxygen atom is converted to aldol:



All the steps are reversible and this accounts for the equilibrium character of the conversions, this being typical of the aldol condensation.

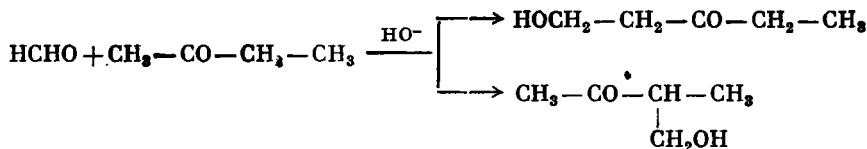
In the reaction between two dissimilar carbonyl compounds each of them may function either as the methylene or as the carbonyl component, as a result of which there can be formed a mixture of products. The preferred direction of the reaction is determined by the mobility of the hydrogen atoms in the α -methylene group and by the tendency of the carbonyl group towards addition.

In the aldehyde-ketone system, the role of the carbonyl component is usually played by the aldehyde, since the aldehyde group is more capable of interacting with the anion of the methylene component:



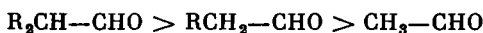
It is obvious that for the side reaction of condensation of two molecules of the aldehyde to be suppressed, an excess of the ketone is required. Unsymmetrical ketones, such as methyl ethyl ketone, can react

across the α -carbon atom of any of the alkyl groups:



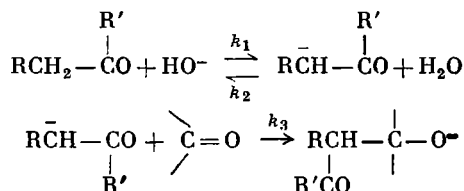
but they react preferentially at the methylene group of the longer carbon chain.

In the aldol condensation of two aldehydes the role of the methylene component is usually played by a grouping with a longer and more branched chain of carbon atoms:



The general cycle of conversions may also involve the product formed; the product of the condensation of carbonyl compounds is a hydroxyaldehyde or a hydroxyketone. This involves the formation of by-product higher-molecular-mass compounds. Besides, the aldols and the starting aldehyde give acetals; the reaction is facilitated in the case of the formation of more stable cyclic acetals—the derivatives of 1,3-dioxane (page 592).

The kinetics of aldol condensation is different for aldehydes and ketones. In the general case, the condensation proceeds in two steps:



In the reaction with aldehydes the second step (the interaction of the anion with the carbonyl group) proceeds rapidly and the overall velocity therefore depends on the rate of formation of the carbanion:

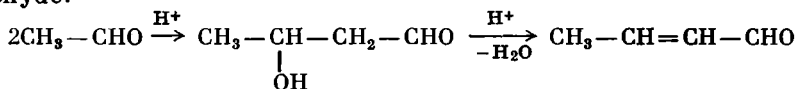
$$r_1 = k_1 \left[\text{RCH}_2 - \underset{\text{R}'}{\overset{|}{\text{C}}} - \text{CO} \right] [\text{HO}^-]$$

On the contrary, in the aldol condensation of ketones their carbonyl group is less liable to undergo addition and the overall rate is determined by the second step, and in the first step there is attained an equilibrium:

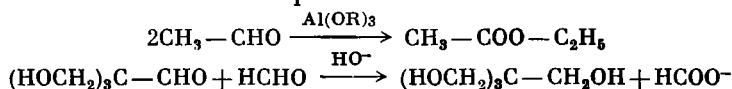
$$\left[\text{RCH} - \underset{\text{R}'}{\overset{|}{\text{C}}} - \text{CO} \right] = K \frac{\left[\text{RCH}_2 - \underset{\text{R}'}{\overset{|}{\text{C}}} - \text{CO} \right] [\text{HO}^-]}{[\text{H}_2\text{O}]}$$

$$r = k_3 [\text{RCH} - \text{COR}'] [\text{RCH}_2 - \text{COR}'] = k_3 K \frac{[\text{RCH}_2 - \text{COR}']^2 [\text{HO}^-]}{[\text{H}_2\text{O}]}$$

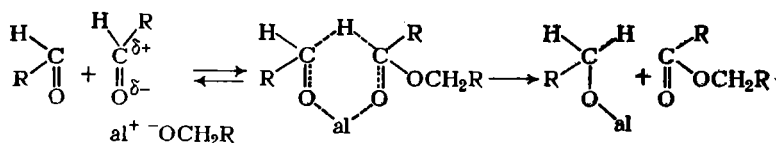
Not infrequently the reactions of aldol condensation can be catalyzed not only by bases but also by acids. In both cases the resultant aldol may immediately split off water, which results in the formation of an unsaturated carbonyl compound, say crotonaldehyde from acetaldehyde:



A special group of reactions closely related to aldol condensation includes some oxidation-reduction (redox) conversions of aldehydes. The catalytic action of strong bases usually brings about aldol condensation, but if this condensation fails to occur because of the specificity of the structure of the aldehyde, then the Cannizzaro reaction takes place, in which one aldehyde molecule is oxidized to a carboxylic acid and the other is reduced to an alcohol. This refers to a greater extent to the catalysis by weak bases (calcium and magnesium alkoxides and especially aluminium alkoxide), which catalyze aldol condensation less strongly but cause oxidation-reduction processes. This involves the formation of an ester in an anhydrous medium (the Tishchenko reaction) and of an alcohol and the salt of an acid in the aqueous medium:

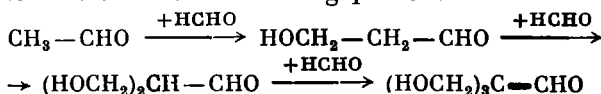


These reactions proceed through a cyclic transition state; the cation of the alkoxide (especially of aluminium alkoxide) exerts an electron-acceptor effect on the carbonyl group with the subsequent attack of the carbonyl carbon atom by the alkoxy ion and with transfer of the hydrogen together with bonding electrons to the other aldehyde molecule:

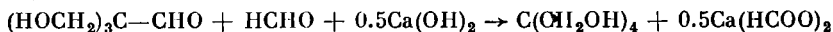


9.4.1. Products Obtained by Aldol Condensation Reactions

Products of the Condensation of Aldehydes with Formaldehyde. Formaldehyde undergoes condensation with acetaldehyde with the successive formation of the following products:

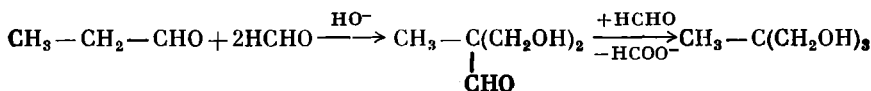


When the reaction is catalyzed by alkalis and an excess of formaldehyde is used, an oxidation-reduction reaction takes place and *pentaerythritol* is formed:

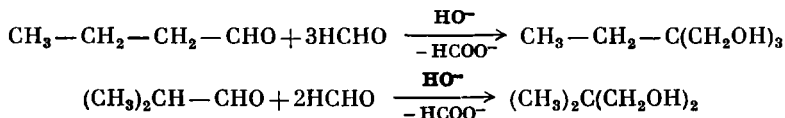


Pentaerythritol is a crystalline substance which melts at 260.5 °C. It has a number of important outlets—it is used for the production of the explosive *penthrite* (pentaerythritol tetranitrate), $\text{C}(\text{CH}_2\text{ONO}_2)_4$, alkyd resins (obtainable by the polycondensation with phthalic anhydride), plasticizers (the esters of pentaerythritol with higher carboxylic acids), and also of a new monomer—bis(chloromethyl)oxacyclobutane and other products.

An analogous route is employed to produce *trimethylolethane* (*pentaglycerine*) from propionaldehyde made by the Oxo synthesis and formaldehyde:



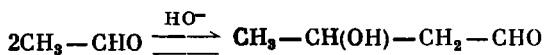
n-Butyraldehyde and isobutyraldehyde give under the same conditions *1,1,1-trimethylolpropane* (*hexaglycerine*) and *2,2-dimethylolpropane*:



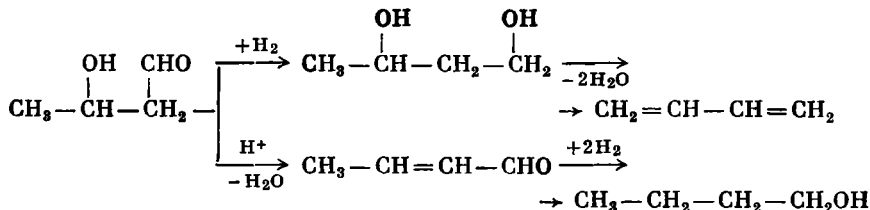
These polyhydric alcohols are rather widely used as substitutes for glycerine and pentaerythritol in the manufacture of alkyd resins and also in the production of plasticizers. The products of the condensation of formaldehyde with higher aldehydes are of little value.

The principal reaction is accompanied by side processes which are mainly associated with the aldol condensation of the starting and intermediate aldehydes, their oxidation-reduction according to the Cannizzaro-Tishchenko reaction and with the formation of acetals (or formals). These side reactions can be suppressed by using an excess of formaldehyde, in which case the second component and the intermediates will react chiefly with formaldehyde. For example, in the synthesis of pentaerythritol 5 moles of HCHO is taken per 1 mole of CH_3CHO (a 25-percent excess), but in this case the yield of the product is only 50-70 percent.

Products of the Condensation of Other Aldehydes. The aldol condensation of acetaldehyde gives *β-hydroxybutyraldehyde*, which is simply called *aldol*:

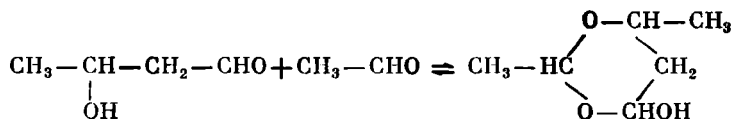


It is still used as an intermediate for the production of 1,3-butanediol, crotonaldehyde and *n*-butyl alcohol. A method of synthesis of butadiene via aldol was once proposed (Ostromyslensky), but it lost its significance:



Of these processes, only the synthesis of *n*-butyl alcohol has retained its commercial significance. It is more economical to produce *n*-butyl alcohol by Oxo synthesis from propylene, CO and H₂, (page 572), but the method involves the co-production of isobutyl alcohol, which does not find wide application. Therefore, the deficit of *n*-butanol is compensated for by its production via acetaldehyde.

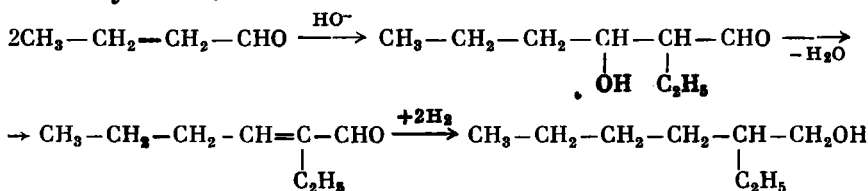
The condensation of acetaldehyde is effected at 20-30 °C in the presence of 0.05 percent of caustic alkali. In order to avoid the formation of higher condensation products, the degree of conversion of acetaldehyde is limited to 40-60 percent. Here, the reaction mass contains not aldol but its cyclic acetal with the starting acetaldehyde (the derivative of 1,3-dioxane):



This acetal is decomposed during distillation into aldol and acetaldehyde. For the successive production of aldol and 1,3-butanediol it is necessary to neutralize the reaction mass very accurately so as to prevent (during distillation) further condensation or elimination of water under the action of acids. The successive synthesis of crotonaldehyde and *n*-butyl alcohol is effected, on the contrary, by acidifying the reaction mass with acetic or phosphoric acid; in this case, upon distillation not only the decomposition of the acetal occurs but also the dehydration of aldol to crotonaldehyde. The distillation of acetaldehyde is followed by the distillation of crotonaldehyde in the form of an azeotropic mixture with 10 percent of water. The yield of the aldehyde may be as high as 90 percent.

Of the products of the condensation and further conversion of aldehydes, 2-ethylhexanol is the most important; its esters are widely used as plasticizers for polymers, as lubricating oils and additives. It is produced by the aldol condensation of *n*-butyraldehyde followed by the dehydration to 2-ethylhexenal, which is then hydrogenated

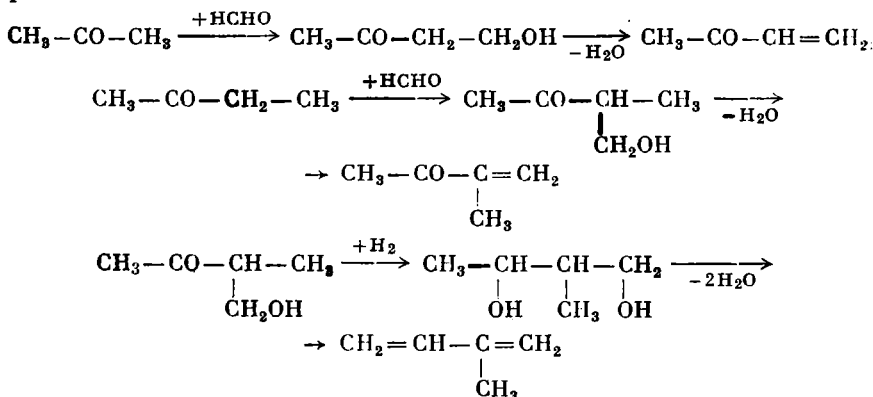
to 2-ethylhexanol:



The by-products formed are the products of the condensation of *n*-butyraldehyde with aldol and an unsaturated aldehyde, the trimers of aldehydes, etc. The usual practice is to combine the first two reactions in a single reactor with the condensation being carried out in the presence of alkali at 90-130 °C. The yield of 2-ethylhexenal is as high as 90 percent.

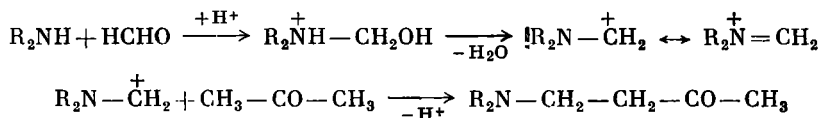
More recent methods of synthesis of 2-ethylhexanol combine the Oxo synthesis of butyraldehydes with aldol condensation and dehydration (the *Aldox process*), in which alkali is added to cobalt carbonyls to catalyze the last two reactions. Another process has also been proposed, which combines hydroformylation, aldol condensation, dehydration and hydrogenation. This can be accomplished in the presence of alkali and also by using cobalt carbonyls modified by tributylphosphine as the catalysts.

Products of the Condensation of Ketones. The condensation of acetone or methyl ethyl ketone with formaldehyde leads to the sequential introduction of methylol groups, but with an excess of ketone in the presence of small amounts of alkali it is possible to stop the reaction at the step of the monomethylol derivative. In turn, in order to prevent the condensation of two molecules of the ketone the degree of conversion of formaldehyde must not be too high. These reactions are commercially important for the synthesis of *vinyl methyl ketone*, *isopropenyl methyl ketone* and partly of isoprene:

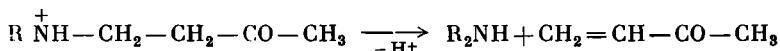


Vinyl methyl ketone and isopropenyl methyl ketone are readily polymerized and are used in the production of plastics.

The best results in the production of these unsaturated ketones are provided by the Mannich reaction, which consists in the condensation of a ketone with formaldehyde and a secondary amine in the presence of acid catalysts:

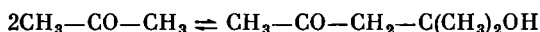


The resultant salt of the Mannich base undergoes cleavage at a higher temperature (100-150 °C) with the liberation of an unsaturated ketone and with the recovery of the secondary amine:



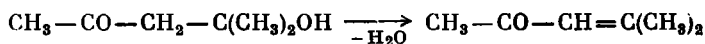
In the reaction with methyl ethyl ketone the attack is directed almost exclusively to the methylene group and isopropenyl methyl ketone is obtained in a high yield.

The condensation of acetone is an industrially important method of synthesis of some valuable compounds. In the presence of a small amount of alkali at a low temperature there is formed *diacetone alcohol*:



which is used as a solvent. The reaction is reversible, the equilibrium degree of conversion being as low as 12 percent at 15-20 °C and 16 percent at 0 °C. Such unfavourable equilibrium conditions are accounted for by the fact that in contrast to aldol condensations of aldehydes, no acetals (which favour the shift of the equilibrium to the right) are formed here. The condensation is carried out at 0-20 °C in the presence of sodium hydroxide or insoluble calcium or barium hydroxides, which are sometimes deposited on supports. The reaction mass is neutralized and distilled; the unconverted acetone is recovered and recycled to condensation.

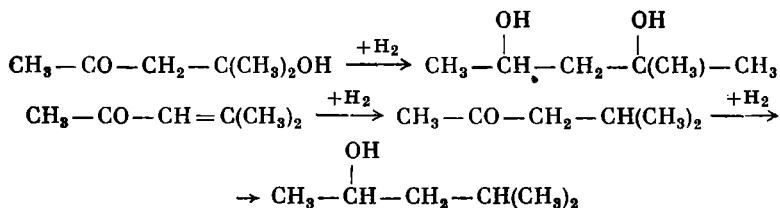
In the presence of an organic acid (say, oxalic acid at 100-120 °C) diacetone alcohol is dehydrated and converted to *mesityl oxide*:



which is used on a modest scale as a solvent.

The hydrogenation of diacetone alcohol and mesityl oxide gives, respectively, 2-methyl-2,4-pentanediol, isobutyl methyl ketone and

isobutyl methyl carbinol:



Of the compounds listed above, *isobutyl methyl ketone* is the most important (it is a liquid; b.p. 116 °C). It is a valuable solvent for varnishes and an extractant used, for example, in the deparaffination of petroleum products. Instead of the three-step synthesis of isobutyl methyl ketone, it has been suggested that the condensation be combined with dehydration in a single reactor with the subsequent hydrogenation of mesityl oxide to isobutyl methyl ketone. A one-step vapour-phase process has also been developed, which employs a bifunctional heterogeneous catalyst (say, Ni on MgO). It gives good results and is in some respects superior to the three- and two-step processes, which are now being abandoned.

9.4.2. Technology of Aldol Condensation Processes

From the example considered above it can be seen that in all interactions of carbonyl compounds with one another the aldol condensation is only one of the steps. The processes based on aldol condensation may be divided into three groups.

1. Processes in which aldol condensation is carried out in a special reactor separately from the subsequent reactions. This step is characterized by a low temperature (0-30 °C), a long reaction time (2-3 hours) and a low degree of conversion of the reagents (10-40 per cent). The low conversion is accounted for by the reversibility of the reaction and by the desire to prevent the successive conversions of the end products. The latter circumstance also calls for the use of reactors close in design to the plug-flow model, say coil reactors. For the aldol condensation of acetaldehyde, which has a suitable boiling point (21 °C), use is made of a tray column fitted with a reflux condenser; the heat of the reaction is dissipated by the evaporation of acetaldehyde with aldol being withdrawn from the still of the column (Fig. 9.7a).

The product passes to hydrogenation (in the production of diols) or, more often, to dehydration and then to hydrogenation (in the production of butyl alcohol from acetaldehyde and of isobutyl methyl ketone from acetone). The product is neutralized accurately by an organic acid and the unconverted reagent is distilled off with the

cyclic acetals being simultaneously decomposed, this being followed by dehydration.

In some cases, it is possible, however, to send the aldol-condensation products directly to dehydration, which is combined with the separation of the water formed, the unconverted reagent and of the dehydration product (Fig. 9.7b). After the aldol condensation is completed the reaction mixture is acidified with an organic acid and the dehydration is carried out at 100-130 °C. Depending on the volatility of the products, the water is either left in the still of the column or is taken as the column overhead together with the reagent.

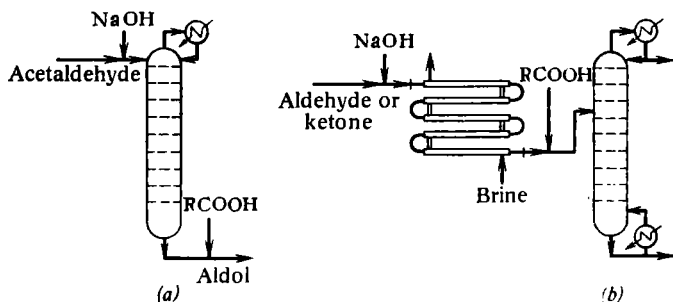


Fig. 9.7. Reaction units for aldol condensation processes:

a—reactor of the tray-column type for aldol condensation of acetaldehyde; b—reaction unit with a tubular reactor for aldol condensation and a tray column for dehydration.

2. Processes in which the aldol condensation is combined (in a single reactor) with the decomposition of cyclic acetals and with the dehydration of aldol. The resultant unsaturated aldehyde is then led to hydrogenation (the production of 2-ethylhexanol). In this case, both reactions are catalyzed by alkalis and carried out at elevated temperature (100-130 °C), which reduces the reaction time (0.5-1 hour). Apart from the intensification of the process and the reduced number of reactors, the process has the following advantages: it is irreversible and it is possible to attain an almost complete conversion of the reagent. Here, the unsaturated aldehyde cannot play the role of the methylene component, which is why even with high conversion the selectivity is sufficiently good. These processes are carried out in various reactors—coil reactors, hollow columns fitted with an external cooler, etc. An example of such technology will be considered below for the case of 2-ethylhexanol production.

Further developments of the combined processes based on aldol condensation are the above-mentioned one-step synthesis of isobutyl methyl ketone, the Aldox process, etc.

3. Processes in which aldol condensation is combined (in a single reactor) with an oxidation-reduction conversion according to the

Cannizzaro-Tishchenko reaction (the synthesis of pentaerythritol, trimethylolethane, hexaglycerine, etc.). A distinctive feature of these processes is the use of a large amount of alkali, which is required to bind the formic acid into a salt. At 30-50 °C the reaction time is 1-2 hours. The batch synthesis is carried out in jacket-cooled stirred reactors equipped with coils; the continuous process is ac-

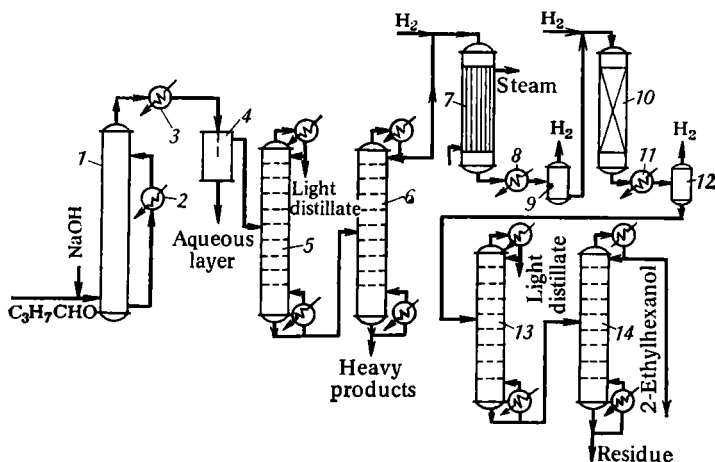


Fig. 9.8. Flow diagram of 2-ethylhexanol production:

1—aldol condensation and dehydration reactor; 2, 3, 8, 11—coolers; 4, 9, 12—separators; 5, 6, 13, 14—fractionating columns; 7, 10—hydrogenation reactors.

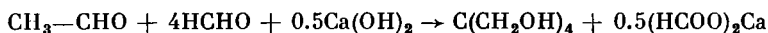
complished in a cascade of such reactors. The technology of processes of this type will be described below for the case of pentaerythritol production.

Production of 2-Ethylhexanol (Fig. 9.8). To *n*-butyraldehyde to be charged to reactor 1 there is added just before the reactor 40-percent NaOH (≈ 0.05 percent). The temperature regime in the reactor (100-130 °C) is maintained by the heat evolved, an excess of which is dissipated by the circulation of the reaction mass through external cooler 2. Aldol condensation and dehydration of aldol take place in the reactor, as a result of which 2-ethylhexenal is formed. The reaction products are chilled in cooler 3, following which they separate in separator 4 into a lower (aqueous) and an upper (organic) layer. The water is led to the stripping of organic compounds and then to purification. The organic layer is subjected to fractionation in columns 5 and 6, the light fraction (unconverted butyraldehyde, water residues, etc.) being distilled off first, followed by 2-ethylhexenal (in vacuum); the heavy by-products are withdrawn from the still of column 6.

The 2-ethylhexenal is then subjected to hydrogenation. In order to avoid the darkening of 2-ethylhexanol and polymeric materials (to which these esters are added as plasticizers) the hydrogenation must be carried out until a high degree of conversion of both the double bonds and the aldehyde groups is attained. For this reason, the hydrogenation is carried out in two steps.

At the first step the process is effected at ordinary pressure in the gas phase over a copper or a copper-chromite catalyst in tubular reactor 7 at 150-170 °C until 97-98 percent conversion is achieved. The products are chilled in cooler 8 and the hydrogen is separated in separator 9. The second step is effected over a nickel catalyst (deposited on kieselguhr or another support) at 150-160 °C and 20-30 MPa. The product from the first hydrogenation step and the preheated hydrogen are passed to reactor 10 containing a fixed catalyst bed. The products are chilled in cooler 11 and the hydrogen is isolated in separator 12. The liquid from the separator is led for fractionation to columns 13 and 14: the light fraction is distilled first and then 2-ethylhexanol is distilled in vacuum. The yield of 2-ethylhexanol is 85-90 percent.

Production of Pentaerythritol. This compound is still produced in some cases by the batch process with calcium hydroxide being used as the condensing agent (in an excess of about 20 percent as compared to the stoichiometric amount):



All the required amount of milk of lime and formalin (in an excess of about 25 percent) are charged into a jacket-cooled stirred reactor fitted with coils, following which an aqueous solution of acetaldehyde is fed gradually (this order of mixing is needed to suppress the side reaction of self-condensation of acetaldehyde). The temperature is gradually raised from 30 to 50 °C. The reaction mass is neutralized with sulphuric acid taken in such an amount that all the calcium ions are combined in the form of the sulphate, which is separated by filtration. The aqueous solution of the products is evaporated, the water and formic acid being distilled off. The mass is then crystallized and the crystals are separated on a filter and recrystallized from the water with addition of activated charcoal. The yield on pentaerythritol is 60-70 percent based on acetaldehyde.

The use of NaOH as the condensing agent has some advantages as compared with calcium hydroxide. When sodium hydroxide is used, only excess alkali can be neutralized after the reaction, and the formate, which is well soluble in water, is separated from pentaerythritol upon crystallization. When trimethylolethane and 1,1,1-trimethylolpropane (hexaglycerine) are to be produced, they are recovered from the water-salt solutions by using an even more convenient method of extraction with an organic solvent.

The flow diagram of the continuous production of pentaerythritol is given in Fig. 9.9. The condensation is carried out in a cascade of jacket-cooled stirred reactors fitted with coils (only two such reactors are shown in Fig. 9.9). An aqueous solution of NaOH and formalin are charged only into reactor 1, and an aqueous solution of acetaldehyde is introduced into each reactor. The liquid overflows from one

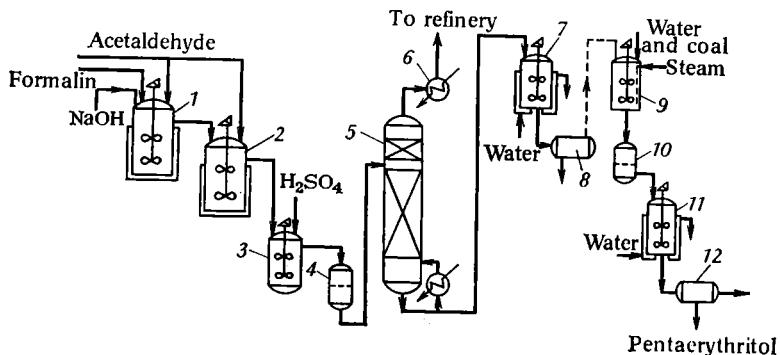
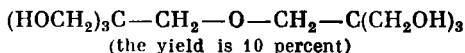


Fig. 9.9. Flow diagram of pentaerythritol production:

1, 2—reactors; 3—neutralization unit; 4, 8, 10, 12—filters; 5—stripping column; 6—condenser; 7, 11—crystallization units; 9—dissolution unit.

reactor into another; the reactors operate at a temperature, which is gradually raised from 30 to 50 °C. The residual caustic soda leaving the last reactor is neutralized with sulphuric acid in neutralizer 3 and the slurry is filtered off on filter 4. The liquid is run to stripping column 5 (or to an evaporator), where the formaldehyde, the methanol contained in it and the major proportion of water are distilled off, condensed in unit 6 and led for processing.

Apart from pentaerythritol, the sirupy liquid from the still of column 5 also contains dipentaerythritol



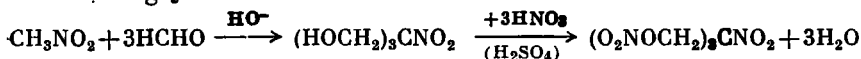
sugary compounds and resins. This sirup is crystallized on cooling, the crude pentaerythritol is filtered and sent for recrystallization with the aid of activated charcoal. To this end, the crude product is dissolved in water upon heating in unit 9, the charcoal is filtered off, the pentaerythritol is crystallized on cooling and filtered off from the mother liquor on filter 12 by washing it with a small amount of water. The resultant pentaerythritol is dried and packaged. The yield of the product is 65-75 percent.

There are plants where the condensation is effected using calcium and sodium hydroxides. In this case, the calcium ions are precipitated from the reaction mixture using sulphuric acid and the insoluble

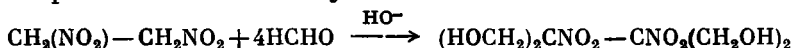
calcium sulphate is filtered off. Only sodium formate is left in the solution, which facilitates the further recovery of pentaerythritol and reduces its loss with the mother liquor.

9.4.3. Other Aldol-Type Reactions

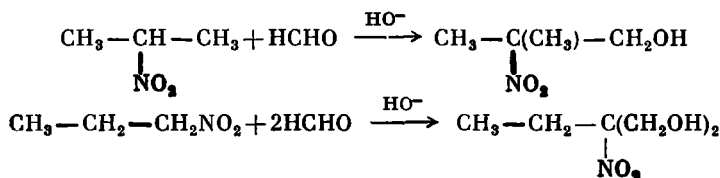
Condensation of Formaldehyde with Aliphatic Nitro Compounds. This is an important route of synthesis of some nitro-alcohols. The reaction proceeds in the presence of 0.1 percent of alkali at room temperature. In this way from nitromethane there is obtained *trimethylolnitromethane*, which on further nitration gives a very powerful explosive—*tri(nitromethylol)nitromethane*, which is more powerful than nitroglycerine:



In an analogous way all the hydrogen atoms in 1,2-dinitroethane are replaced and tetramethyloldinitroethane is formed:

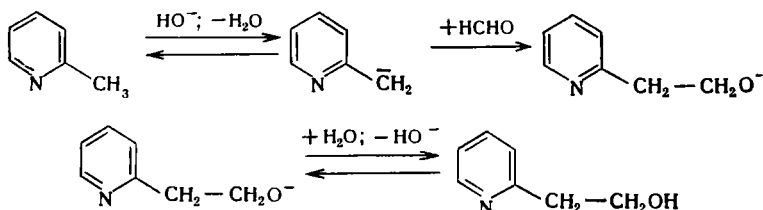


2-Nitropropane gives only a monomethylol derivative and 1-nitropropane only a dimethylol derivative:

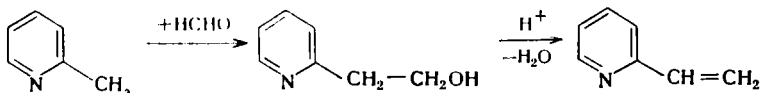


These and similar nitro-alcohols are of practical value as intermediates in the syntheses of some aminoalcohols (by hydrogenation) and the esters of carboxylic acids and phosphoric acid, which appear to be good plasticizers. The technology of the reaction of formaldehyde with nitroparaffins does not differ substantially from that of aldol condensation processes.

Synthesis of Vinylpyridines. 2- and 4-Alkylpyridines are the analogues of carbonyl and nitro compounds in regard to aldol condensation. They are pseudoacids and are condensed with formaldehyde in the presence of alkali, forming methylol derivatives:

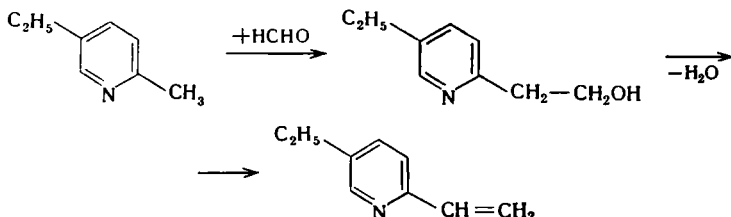


The reaction is effected in the same way as other aldol condensations. The resultant alcohol readily splits off water in the presence of acid-type catalysts; in this way *2-vinylpyridine* is produced from α -picoline on an industrial scale



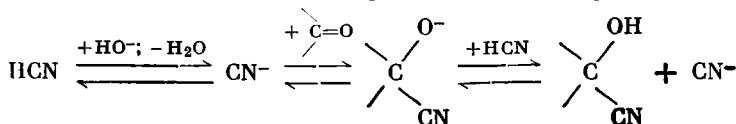
and *4-vinylpyridine* from γ -picoline.

The above-mentioned 2-methyl-5-ethylpyridine reacts in the same way to give *2-vinyl-5-ethylpyridine*:



These vinylpyridines are valuable monomers for the manufacture of synthetic rubbers and other polymeric materials.

Production of Cyanohydrins. The synthesis of cyanohydrins from aldehydes or ketones and HCN is analogous to aldol condensation processes; it is also catalyzed by bases and is a reversible exothermic reaction which proceeds according to the following scheme:



When acetonecyanohydrin is to be obtained from acetone and HCN, the equilibrium conditions at 25 °C correspond to the 11.5-percent degree of its dissociation into acetone and hydrocyanic acid (hydrogen cyanide). Cyanohydrins therefore decompose in the presence of bases or at elevated temperature and always contain impurities of the starting compounds.

The catalysts used in industrial practice are small amounts of concentrated solutions of sodium hydroxide or sodium carbonate and the reaction is carried out in the temperature range from 0 to 40-50 °C. Just as with other reversible exothermic reactions, the process must be carried out so as to maintain a higher temperature when the system is still far from equilibrium. On the contrary, at the final stages it is necessary to cool the reaction mass, which favours the shift of the equilibrium to the side of cyanohydrin formation.

One of the typical reaction units employed for the production of cyanohydrins, which can equally well be used for reversible aldol condensations, is given in Fig. 9.10. The unit consists of two parts—a tray column 1 and a tubular cooler 2. The reagents and the catalyst are charged to the upper tray, and the reaction mass overflows into the tubes of the cooler. Here it is gradually cooled; at a low temperature there is attained a high degree of conversion of hydrogen cyanide (90 percent and higher). Because of the high volatility of HCN the reactor is fitted with a condenser 3 cooled by brine. The reaction mass is then neutralized with sulphuric acid and the unconverted hydrogen cyanide and acetone are distilled off from it and returned to synthesis. This production is dangerous because of the high toxicity of hydrogen cyanide and therefore an effective system for ventilation, trapping and purification of the effluent gases containing hydrogen cyanide is required and the apparatus must be well sealed.

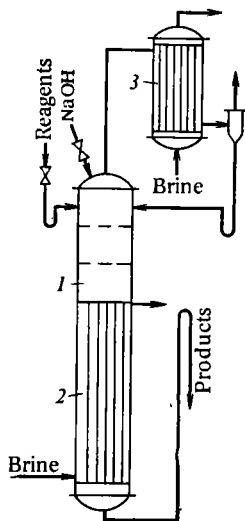
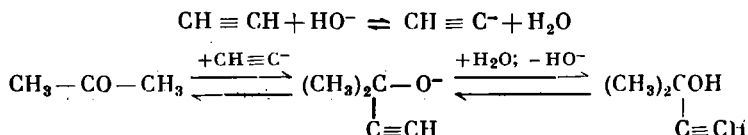


Fig. 9.10. Reaction unit for production of cyanohydrins:

1—tray column; 2—tubular cooler; 3—reflux condenser.

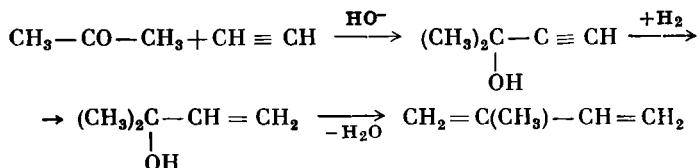
method of production of these compounds is still widely employed on an industrial scale: lactic acid is produced from acetaldehyde and methyl methacrylate from acetone (page 240), etc.

Reactions of Carbonyl Compounds with Acetylene. In contrast to the syntheses from acetylene encountered earlier, its condensation with carbonyl compounds proceeds with retention of the triple bond and with the formation of acetylene alcohols (*ethynylation* or *alkynol synthesis*). In the case of ketones the process is catalyzed by alkalis and proceeds through the intermediate formation of acetylenides, which are strong nucleophiles capable of addition at the carbonyl group:



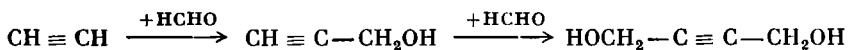
This is accompanied by the condensation of two ketone molecules and therefore in order to increase the yield of the end product it is better to carry out the process in solution under acetylene pressure for the ketone concentration to be relatively low and the acetylene concentration high.

This reaction, which is known as the Favorsky reaction, is employed on an industrial scale for the synthesis of some acetylene alcohols and their conversion products. It has recently been carried out for the production of isoprene from acetylene and acetone:

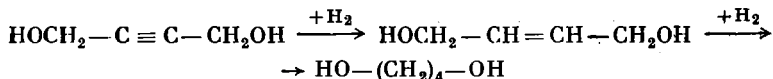


The synthesis of dimethyl ethynyl carbinol is carried out in the medium of liquid ammonia at 20-40 °C and 2 MPa. The yield of isoprene is 90 percent, but because of the use of the expensive raw material this method is not in much favour.

The condensation of acetylene with aldehydes in the presence of bases as the catalysts does not give a positive result because of the predominant occurrence of the aldol condensation of aldehydes. Reppe carried out this condensation reaction with the aid of a new catalyst based on copper acetylenide. In this way, from acetylene and formaldehyde there are successively formed propargyl alcohol and 1,4-butyne-1,3-diol:



1,4-Butynediol is hydrogenated to give 1,4-butenediol and 1,4-butanediol:



The synthesis is carried out using oxides of copper and bismuth deposited on a porous support at 85-90 °C and 0.1-0.6 MPa. The method is chiefly employed for the production of 1,4-butanediol, but today there are more economical methods of manufacture of this product (page 485).

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